

(NASA-CR-139364) ADVANCED TECHNIQUES FOR  
DETERMINING LONG TERM COMPATIBILITY OF  
MATERIALS WITH PROPELLANTS Final Report,  
21 Jun. (Boeing Aerospace Co., Seattle,  
Wash.) 223 p HC \$14.25 CSCI 211

N74-30233

Unclas

G3427 16718

D180-14839-2

ADVANCED TECHNIQUES FOR DETERMINING  
LONG TERM COMPATIBILITY OF  
MATERIALS WITH PROPELLANTS

FINAL REPORT

DECEMBER 1973

Prepared For

THE JET PROPULSION LABORATORY  
PASADENA, CALIFORNIA 91103

UNDER NATIONAL AERONAUTICS AND SPACE ADMINISTRATION  
CONTRACT NAS7-789

By

Richard L. Green, James P. Stebbins,  
Alan W. Smith and Kent E. Pullen

THE BOEING AEROSPACE COMPANY  
RESEARCH AND ENGINEERING DIVISION  
SEATTLE, WASHINGTON 98124

## FOREWORD

This contract report was prepared by the Boeing Aerospace Company, Seattle, Washington, and describes work accomplished during the period from June 21, 1972 to December 15, 1973. The original program began in August, 1970 with the first phase of the work reported in June 1972. The program was managed by the Jet Propulsion Laboratory of the California Institute of Technology under the technical direction of Mr. Louis R. Toth. The NASA Advanced Technology Program Manager was Mr. William Cohen, Code RPT, Office of Aeronautics and Space Technology, Washington, D.C.

The work performed on this program was accomplished by the Research and Engineering Division of the Boeing Aerospace Company with technical direction provided by the Rocket Propulsion Staff of Aero/Propulsion Engineering. The technical team was headed by Dr. R. L. Green with Mr. J. R. O'Brien as Program Manager.

Acknowledgement is gratefully given to the following technical personnel who supported this program:

Mr. A. E. Lawler	-	Hydrazine Analysis
Dr. K. E. Pullen	-	Various Experimental Assistance
Dr. A. W. Smith	-	Surface Impedance Demonstration
Mr. B. L. Smith	-	Atomic Absorption Analyses
Mr. T. L. Smith	-	Hydrazine Flow Tests
Mr. J. P. Stebbins	-	Hydrazine Immersion Tests
Mr. J. C. Thomas	-	Atomic Absorption Analyses

Further acknowledgement is given to Mr. N. J. Roberts, of the Lawrence Livermore Laboratory for the neutron activation analyses.

## TABLE OF CONTENTS

	Page
1.0 INTRODUCTION AND SUMMARY . . . . .	1
1.1 Program Objectives . . . . .	2
1.2 Specific Tasks . . . . .	3
1.3 Summary. . . . .	6
2.0 THE PREDICTION METHOD. . . . .	9
2.1 General Flow Chart . . . . .	9
2.2 Detailed Immersion Test. . . . .	23
2.3 Establishing the Kinetic Rate Expression . . . . .	28
2.4 Using the Prediction Method. . . . .	35
3.0 DESCRIPTION -- ADVANCED TECHNIQUES . . . . .	39
3.1 Neutron Activation Analysis. . . . .	39
3.1.1 Theory . . . . .	39
3.1.2 Practical Considerations . . . . .	41
3.1.3 Equipment. . . . .	41
3.1.4 Experimental Procedures of the Dry Activation Analysis Technique. . . . .	43
3.1.5 Detection Sensitivity Limits . . . . .	43
3.2 Radioactive Tracer Technique . . . . .	47
3.2.1 Theory . . . . .	47
3.2.2 Practical Considerations . . . . .	47
3.2.3 Equipment. . . . .	47
3.2.4 Experimental Procedures. . . . .	47
3.2.5 Detection Sensitivity Limits . . . . .	49
3.3 Atomic Absorption Spectroscopy With Graphite Tube Furnace Sampler . . . . .	51
3.3.1 Theory . . . . .	51
3.3.2 Practical Considerations . . . . .	51
3.3.3 Equipment. . . . .	52
3.3.4 Experimental Procedures. . . . .	52
3.3.5 Detection Sensitivity Limits . . . . .	54
3.3.6 Discussion of Errors . . . . .	54



## TABLE OF CONTENTS (Continued)

	Page
4.0 EXPERIMENTAL VERIFICATION OF THE PREDICTION METHOD. . . . .	57
4.1 The 6Al-4V Titanium/Liquid Fluorine System. . . . .	57
4.1.1 System Definition and Application . . . . .	57
4.1.2 Preliminary Exposure Test . . . . .	58
4.1.3 Determining the Rate of Metal Buildup in $LF_2$ . . . . .	59
4.1.4 Correlation of Metal Buildup to Propellant - Material Interaction . . . . .	69
4.1.5 Integration of Results. . . . .	74
4.1.6 Development of the Kinetic Rate Expression. . . . .	77
4.1.7 Predicted Long Term Behavior. . . . .	78
4.2 The 6Al-4V Titanium/FLOX (88:12) System . . . . .	78
4.2.1 System Definition and Application . . . . .	79
4.2.2 Preliminary Exposure Test . . . . .	79
4.2.3 Determining the Rate of Metal Buildup in FLOX . . . . .	80
4.2.4 Correlation of Metal Buildup to Propellant - Material Interaction. . . . .	80
4.2.5 Integration of Results. . . . .	84
4.2.6 Development of the Kinetic Rate Expression. . . . .	84
4.2.7 Predicted Long Term Behavior. . . . .	84
4.3 The 2219-T87 Aluminum/Liquid Fluorine System. . . . .	86
4.3.1 System Definition and Application . . . . .	86
4.3.2 Preliminary Exposure Test . . . . .	86
4.3.3 Determining the Rate of Aluminum Buildup in $LF_2$ . . . . .	87
4.3.4 Correlation of Aluminum Buildup to Propellant - Material Interaction. . . . .	92
4.3.5 Integration of Results. . . . .	95
4.3.6 Development of the Kinetic Rate Expression. . . . .	95
4.3.7 Predicted Long Term Behavior. . . . .	95
4.4 The 6Al-4V Titanium/Hydrazine System. . . . .	98
4.4.1 System Definition and Application . . . . .	98
4.4.2 Preliminary Exposure Test . . . . .	99
4.4.3 Determination of the Rate of Metal Buildup in the 6Al-4V Titanium/Hydrazine System . . . . .	99
4.4.4 Correlation of Metal Buildup to Propellant - Material Reaction . . . . .	108

## TABLE OF CONTENTS (Continued)

	Page
4.5 The 304L CRES/Hydrazine System. . . . .	111
4.5.1 System Definition and Application. . . . .	111
4.5.2 Preliminary Exposure Test. . . . .	112
4.5.3 Determination of the Rate of Metal Buildup in the 304L CRES/Hydrazine . . . . .	112
4.5.4 Correlation of Metal Buildup to Propellant- Material Reaction. . . . .	121
4.6 Monomethylhydrazine Studies . . . . .	132
5.0 FEASIBILITY DEMONSTRATION OF THE USE OF ELECTRICAL IMPEDANCE MEASUREMENTS TO DETERMINE THE EFFECT OF HYDRAZINE ON ALUMINUM SURFACES . . . . .	135
5.1 Introduction . . . . .	135
5.2 Theoretical Background . . . . .	136
5.3 Experimental Demonstration. . . . .	138
5.4 Experimental Results. . . . .	141
5.5 Conclusions . . . . .	147
6.0 HYDRAZINE MONOLAYER BUILDUP TESTING. . . . .	149
6.1 Background. . . . .	149
6.2 Experimental Program. . . . .	149
6.3 Experimental Results and Discussion . . . . .	151
7.0 CONCLUSIONS. . . . .	163
8.0 RECOMMENDATIONS. . . . .	167
9.0 REFERENCES . . . . .	171
APPENDIX A JANNAF Liquid Propellant Test Number 726.0 - Static Immersion. . . . .	175
APPENDIX B Procedure for Analysis of Residue in FEP Teflon Tubes . . . . .	213

## ILLUSTRATIONS

Figure		Page
1-1	Overall Program Development . . . . .	4
2-1	Overall Prediction Method . . . . .	10
2-2	Determination of Rate of Pressure Rise. . . . .	13
2-3	Detailed Immersion Test . . . . .	14
2-4	Determination of Rate of Metal Buildup. . . . .	16
2-5	Determination of Rate of Surface Degradation. . . . .	19
2-6	Anion Penetration by Surface Etching. . . . .	21
2-7	Measure Surface Alteration by Surface Impedance . . . . .	22
2-8	Compatibility Program Functional Matrix . . . . .	24
2-9	Establishing the Kinetic Rate Expression. . . . .	29
2-10	Linear Plot for a First-Order and Second-Order Reaction . .	31
2-11	Curve Shapes for Various Reaction Rates . . . . .	34
2-12	Dependence of Reaction Rate on Temperature. . . . .	35
3-1	Neutron Activation Analysis . . . . .	42
3-2	Dry Activation Analysis Technique . . . . .	44
3-3	Radioactive Tracer Experimental Procedure . . . . .	48
3-4	Perkin-Elmer Atomic Absorption Spectrometer With Graphite Furnace . . . . .	53
4-1	Test Configuration for 6Al-4V Titanium Fluorine/FLOX Systems.	63
4-2	Preparation of the FEP Teflon Container for Fluorine/FLOX Systems . . . . .	63
4-3	Storage Container for 6Al-4V Titanium/Fluorine System . . . .	64
4-4	Fluorine Oxidizer Handling System . . . . .	66
4-5	View of 6Al-4V Titanium/Liquid Fluorine Test Setup. . . . .	67
4-6	Titanium Concentrations in Liquid Fluorine, Dependence on HF and Time. . . . .	71
4-7	Rate of Titanium Buildup in Liquid Fluorine As A Function of HF Concentration Assuming Zero-Order Kinetics. . . . .	76
4-8	Titanium Buildup in Liquid Fluorine at 77.7°K as a Function of Time Assuming Zero-Order Kinetics. . . . .	76
4-9	Titanium and Vanadium Concentrations in FLOX, Dependence on HF and Time . . . . .	83

# ILLUSTRATIONS (Continued)

Figure		Page
4-10	2219 Aluminum Test Configuration . . . . .	89
4-11	2219 Aluminum Specimen Coupon . . . . .	89
4-12	Overall Test Setup, 2219 Aluminum/Liquid Fluorine. . . . .	90
4-13	Close Up of Setup in Counting Configuration. . . . .	90
4-14	Metal Buildup in Liquid Fluorine With Time From Contact With 2219 Aluminum . . . . .	94
4-15	Derivation of the Rate Constant for Aluminum Buildup in Liquid Fluorine . . . . .	96
4-16	Temperature Dependence of the Rate Constant. . . . .	96
4-17	Exposure Capsule and 6Al-4V Titanium Specimen. . . . .	102
4-18	Array of Capsules in the Wooden Exposure Block . . . . .	102
4-19	Nitrogen-Purged Plastic Enclosure Used for all Hydrazine Transfer Operations. . . . .	106
4-20	Constant-Temperature Ovens and Recorder. . . . .	106
4-21	Equipment for the Preparation of CO <sub>2</sub> - Doped Hydrazine . . . . .	115
4-22	Comparison Between Theoretical and Experimental Buildup of Iron in the 304L CRES/Hydrazine System. . . . .	126
4-23	Precipitate Formation in the 304L CRES/Hydrazine System. . . . .	129
5-1	Impedance Measuring Cell . . . . .	140
5-2	Hydrazine Exposure Cell. . . . .	142
5-3	Decrease in Impedance, $\Delta Z$ , Due to Hydrazine Exposure Versus Initial Impedance, $Z_p$ . . . . .	144
5-4	Anodizing Current Versus Anodizing Voltage . . . . .	146
6-1	Standard Flow System Hardware. . . . .	150
6-2	Close-up of Screen Filter Area . . . . .	150
6-3	Flow Test Involving Water With Iron-59 Tracer Added. . . . .	153
6-4	Flow Test Involving Hydrazine With Iron-59 Tracer Added. . . . .	154
6-5	Flow Test Involving Hydrazine with 1.9 Parts Per Million Dissolved Iron Added in Addition to Iron-59 Tracer . . . . .	155
6-6	Flow Test Involving Hydrazine With Zinc-65 Tracer Added. . . . .	156

# TAPLES

Table	Page
3-1 Sensitivities in the Graphite Tube Furnace AAS . . . . .	54
4-1 Possible Container Materials for Titanium/Liquid Fluorine Test. . . . .	60
4-2 Test Conditions for 6Al-4V Titanium/LF <sub>2</sub> System . . . . .	65
4-3 Test Results for 6Al-4V Titanium in LF <sub>2</sub> . . . . .	70
4-4 Average Rate of Titanium Buildup in Liquid Fluorine at 77.7°K . . . . .	77
4-5 Test Conditions for 6Al-4V Titanium in FLOX. . . . .	81
4-6 Test Results, 6Al-4V Titanium in FLOX. . . . .	82
4-7 Average Rate of Titanium Buildup in FLOX at 77.7°K . . . . .	85
4-8 Chemical Composition of 2219-T87 Aluminum. . . . .	86
4-9 Test Conditions for 2219-T87 Aluminum/Liquid Fluorine System . . . . .	93
4-10 Mass of 2219-T87 Aluminum Samples Before and After Exposure to Liquid Fluorine . . . . .	93
4-11 Chemical Composition of 6Al-4V Titanium Specimens. . . . .	100
4-12 Analysis of Hydrazine, Drum No. H-108. . . . .	102
4-13 Atomic Absorption Spectroscopy Results, 6Al-4V Titanium/Hydrazine. . . . .	110
4-14 Chemical Composition of 304L CRES Specimens. . . . .	113
4-15 Atomic Absorption Spectroscopy Results, 304L CRES/Hydrazine. . . . .	122
4-16 Monomethyl Hydrazine Exposure Summary. . . . .	133
6-1 Flow Test Involving Water With Iron-59 Tracer Added. . . . .	157
6-2 Flow Test Involving Hydrazine With Iron-59 Tracer Added. . . . .	158
6-3 Flow Test Involving Hydrazine With 1.9 Parts Per Million Dissolved Iron Added in Addition to Iron-59 Tracer . . . . .	160
6-4 Flow Test Involving Hydrazine With Zinc-65 Tracer Added. . . . .	161

## 1.0 INTRODUCTION AND SUMMARY

High reliability has been the byword of the U. S. space program since its inception. Reliability took on a special meaning beginning with the Mercury program wherein man first explored the harsh unknowns of space. When human life is at stake, the requirements for reliability become high indeed.

For unmanned spacecraft, the payload is not so precious as that of the manned version but the mission durations are becoming longer and the total financial investments are becoming higher. If the unmanned mission is to be a success, the mission must be completed, 100%. So now the question is not just one of high reliability but one of long-term reliability.

The propulsion system of the long mission spacecraft has a unique responsibility: operate reliably in the space environment for long periods of ten to fifteen years but on an intermittent duty cycle basis of perhaps only once per year. One of the most critical factors which determines whether or not the propulsion system can continue to operate reliably is the complete compatibility of the propellant with the materials of construction.

Complete compatibility can be defined as a state wherein even subtle interactions will not cause deleterious events over the term of the mission involved. Often the time from program inception to launch date is less than the length of the mission. The desire to use the latest materials of construction means that the design engineer must use short-term experimental data for qualification purposes instead of real-time data. This leads to doubts concerning the serviceability for long missions and causes engineers to over design and provide backup components. These both cause added cost and added weight.

The solution to the dilemma is to develop the techniques and methodology whereby short-term data can be used to make reliable long-term predictions of propellant-material compatibility.

## 1.1 PROGRAM OBJECTIVES

The objective of this effort was to advance the art of techniques for qualifying materials and propellants used on chemical liquid propulsion feed systems required for unmanned space exploration vehicles. The materials were to be used with earth storable and space storable propellants at pressures up to 1000 psi and operate reliably in the space environment for periods of ten to fifteen years but on an intermittent duty cycle basis; for example, one or more duty cycles per year during the mission life.

The techniques developed to meet the objectives were required to yield data in a much shorter time than the mission life. Accurate compatibility and reliability assessments could be assigned by means of extremely sensitive measurements of the malefic effects of the propellant on the material, and conversely the effects of the material exposure on the propellant. The words "materials and compatibility" were taken in the broadest sense such as to include: source, processing, storage, flight type usage, etc.

The scope of the work included analyses, design, feasibility experimentation, and technical demonstration.

Materials considered were related to the following liquid propulsion feed system functions:

- a. Flow shut off valves
- b. Isolation type valves
- c. Flow metering or throttling devices
- d. Regulators for cold gases
- e. Regulators for hot gases
- f. Vent or relief valves
- g. Fill or service valves
- h. Filters
- i. Tankage and propellant acquisition devices
- j. Lines and service connections

Primary emphasis was given to the propellants hydrazine, monomethylhydrazine, diborane, oxygen difluoride, FLOX, and liquid fluorine.

## 1.2 SPECIFIC TASKS

The program was divided into two phases. The first phase consisted of an examination and development of testing methods and sensitive measurement techniques and was reported fully in an interim report [1-1]\*. The second phase involved the application of the testing methods and sensitive techniques to the development of a method of predicting long-term interaction between propellants and materials using short-term data. The results of the latter phase are reported in this volume. The overall program is shown in Figure 1-1.

The elements of the first phase of the program consisted of the following tasks.

### Existing Technology Survey

A comprehensive survey was performed of the existing technology of methods, measurements, and testing techniques for qualifying liquid propulsion material-propellant combinations for spacecraft applications. Those which, as currently practiced, would contribute and provide meaningful results towards determining material-propellant compatibility, performance, and reliability for long mission durations of ten to fifteen years in space and planetary environments within the solar system were identified.

### Evaluation of Existing Technology

After completion of the survey, a critical evaluation of the existing techniques was made to determine if any of them could be refined sufficiently to meet the requirements. Areas of improvement were noted.

### Development of New Technology

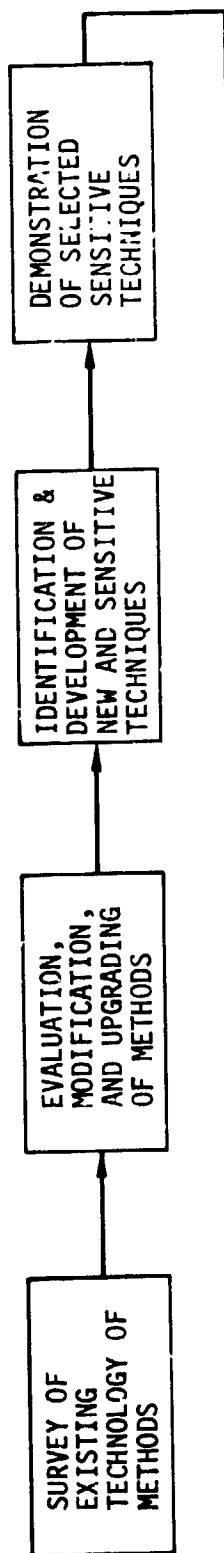
Part of the program effort was devoted to investigating the feasibility and advantages of developing and utilizing new methods to achieve significant improvements over existing ones. Areas requiring technology advancement were also defined.

---

\* Numbers in brackets refer to references listed in Section 9.



PHASE I



PHASE II

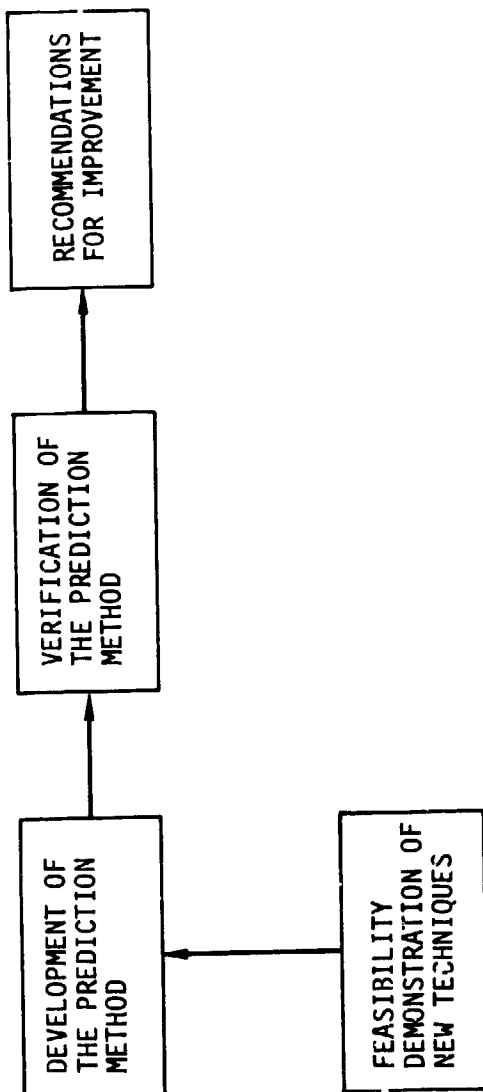


FIGURE 1-1: OVERALL PROGRAM DEVELOPMENT

### Experimental Demonstration

A complete experimental demonstration of one or more of the techniques identified in the preceding task was accomplished. A test program was conducted that gave reliable evidence that the information obtained was directly correlatable with extended periods of time, and gave reliable evidence that the basic program requirements were met assuring satisfactory spacecraft service.

The details of the second phase of the program consisted of the following tasks.

### Development of the Prediction Method

The objective of the task was to establish the detailed methods and procedures which would be required to predict propellant-material compatibility for periods of time up to ten years with a high degree of certainty. The sensitive measurement techniques identified in the first phase of the program were to be used as a foundation for the method. The task was directed toward the development and establishment of an analytical method which can be used for qualifying candidate propellant-material combinations.

### Verification of the Prediction Method

An integral part of the development of the prediction method was the orderly laboratory verification of that method. The laboratory testing played an important role in the modification or addition to the method to produce the best possible tool. Laboratory data was to be generated for the materials 6Al-4V titanium and 2219-T87 aluminum with the oxidizers: FLOX (88:12) and liquid fluorine and with the fuels: hydrazine and monomethylhydrazine. For the laboratory testing with the fuels, 304L CRES was substituted for the 2219-T87 aluminum.

### Feasibility Demonstration of New Techniques

Several techniques identified under the first phase of work which showed promise of a capability for detecting subtle changes were to be assessed on a limited basis.

### Propellant Monolayer Buildup Investigation

Previous work [6-1] with hydrazine propellant indicated that there was evidence of a "monolayer" buildup on a filter screen test specimen. This ancillary task was to investigate this phenomenon in sufficient depth to determine the significance of this "monolayer" buildup for hydrazine type propellants. It was to be established whether the deposition was limited to a monolayer, or whether increased time or the presence of metal contaminants or specific impurities would promote additional deposition to a point where component performance degradation would result.

#### 1.3 SUMMARY

A method for the prediction of propellant-material compatibility for periods of time up to ten years has been developed. The method utilizes a system of flow diagrams showing analysis paths, decision points, and required data inputs. The method also relies on a foundation of basic chemical kinetics to make predictions about interactions in the future from accurate short-term data.

The laboratory test program produced results that were extremely valuable on their own merits in addition to providing data needed for the checking and verification of the prediction method. It was established that hydrogen fluoride impurity in fluorine plays an important role in the long-term compatibility of liquid fluorine with 6Al-4V titanium. On the other hand, 2219-T87 aluminum was relatively unaffected by liquid fluorine with hydrogen fluoride present. The action of FLOX (88:12) on 6Al-4V titanium was found to be essentially the same as that of liquid fluorine. Predictions on the amount of metal buildup in the propellant (and thus the overall compatibility of the combinations) were made using the prediction method. These predictions indicated excellent compatibility for the terms of interest especially if the hydrogen fluoride content in the propellant is reduced to a low level.

The testing with the fuels hydrazine and monomethylhydrazine was equally fruitful. Two systems were chosen which were capable of

illustrating the prediction method in an elegant manner: (1) the 6Al-4V titanium in hydrazine propellant with chlorine impurity present, and (2) the 304L CRES in hydrazine with carbon dioxide impurity present. It was established that chlorine present as metal chloride in hydrazine produced no deleterious interaction with the titanium and that hydrazine should be compatible with 6Al-4V titanium for a period of time much longer than the time of interest.

It was also found that corrosion of 304L CRES by hydrazine with carbon dioxide added was best explained by a two part mechanism: (1) a comparatively slow zero-order reaction during which time dissolution of the protective metal oxide occurred followed by (2) a first-order reaction with respect to the  $\text{CO}_2$  concentration. There may exist a difference in reactivity of the hydrazine system depending on whether the  $\text{CO}_2$  is present as active hydrazinium carbazate or as inactive metallic carbazate.

It was concluded that the prediction method should prove to be an extremely valuable and viable tool and that there are yet areas needing further development.

## 2.0 THE PREDICTION METHOD

The steps, techniques, procedures, decisions, and theory used to arrive at recommendations for long-term service of certain materials with propellants comprise a method which we choose to term a prediction method. The basic concept is to generate short-term data using sensitive measurement techniques and, using the method, make an accurate prediction concerning the performance over the long term. Whereas some parts of the method may be obvious or merely common sense, other parts embark into new territory in so far as material propellant compatibility testing is concerned. This prediction method attempts to draw together into a coordinated plan the individual parts and procedures which may have been utilized in the past along with modified techniques and/or new approaches to cracking the puzzle of subtle interaction and long-term servivibility.

### 2.1 THE GENERAL FLOW CHART

Shown in Figure 2-1 is an overall representation of the flow path utilized in making a long-term prediction from short-term data. This chart will be described in detail but note that the ultimate success of the method relies on the ability to define the kinetic rate expression that describes the interaction between propellant and material. Without this expression, an exact prediction cannot be made. Bear in mind, however, that the inability to develop such an expression may indicate such a low level of interaction that satisfactory performance is assured. Also, it may be possible to derive an expression for the maximum possible rate of reaction from which an upper limit to the degree of interaction can be established.

The basic foundation of the method is the static immersion test but this does not preclude the need for other forms of testing such as dynamic and ignition tests. This prediction method shown in Figure 2-1 and associated sub-charts represents the best model now available. It is intended that this be a viable method and as such now represents the infant state of development.

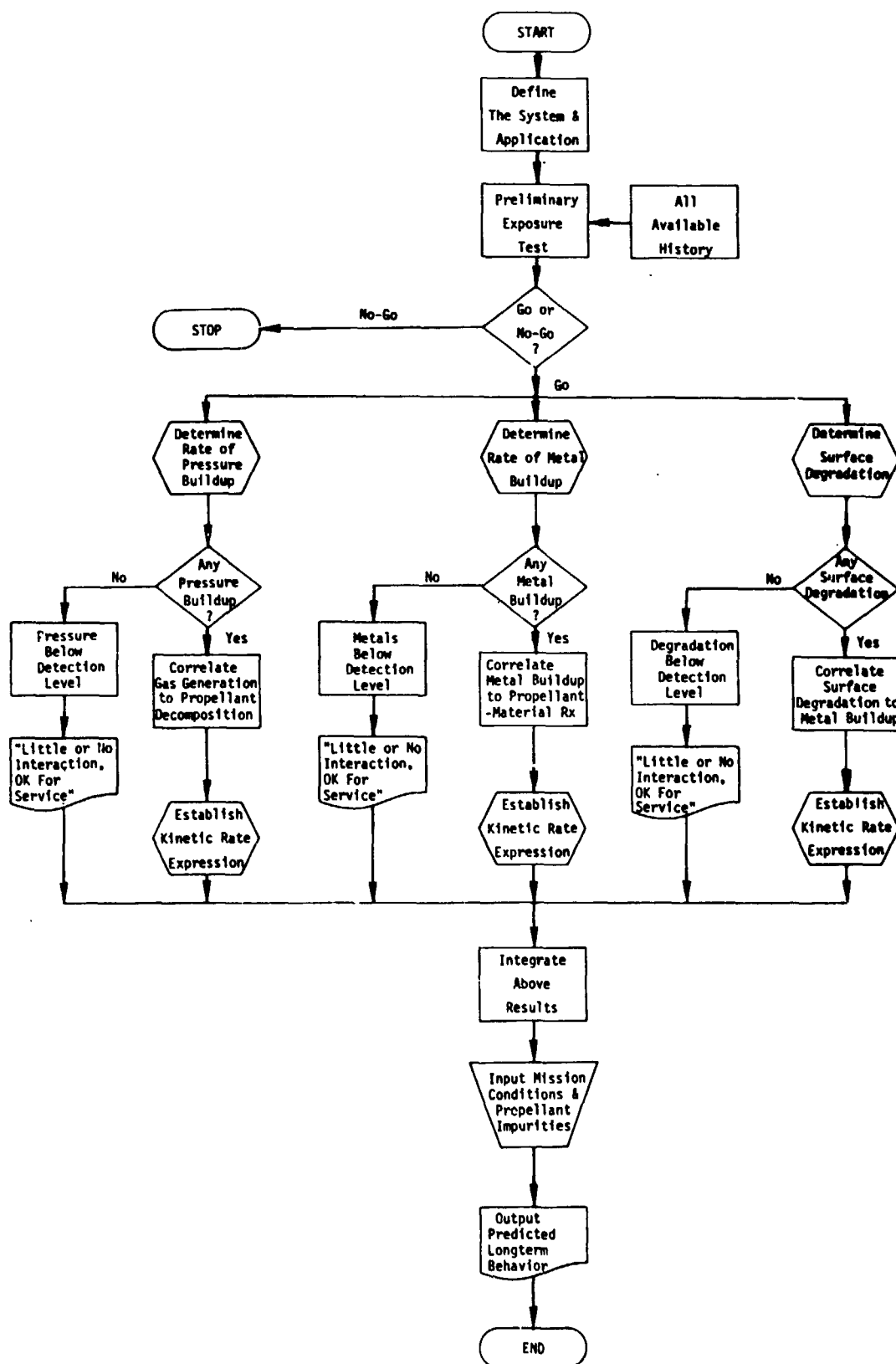


FIGURE 2-1: OVERALL PREDICTION METHOD

The method begins with a complete definition of the propulsion system and the application for which it is being considered. This would include description of such items as tanks, lines, valves, actuators, propellant acquisition devices and transducers. The description would include the alloy type, service life expected, operational pressure and temperature, and environmental parameters such as zero gravity, radiation sources, shock and vibration, thermal cycling, thermal shock and vacuum.

This sets the stage for the next step which is the preliminary immersion (or exposure) test. In practice, this test may not be necessary because of existing data for the system that would allow the subsequent go/no-go decision to be made. However, it may be prudent to establish shock sensitivity or other parameters indicative of gross incompatibility.

Once it is established that the propellant-material pair is tacitly compatible, one can proceed to determining the degree of subtle interaction as shown in the three legs below the go/no-go decision block. These logic paths describe the process used to establish the existence of a pressure build-up due to propellant decomposition, a metal build-up in the propellant due to reaction of propellant with the material, and material surface degradation for the same reason. The paths will be referred to as the pressure leg, the metal leg, and the surface leg, respectively.

#### 2.1.1 Determining the Rate of Pressure Build-up

Certain chemical propellants decompose to yield gaseous products (viz.  $N_2H_4$ , MMH,  $H_2O_2$ ,  $B_2H_6$ ) that, if allowed to build up, would cause a dangerous situation and/or degrade propellant performance beyond acceptable limits. Propellant decomposition can be caused by metal surface catalysis, elevated temperatures, propellant impurities, and combinations of these. A knowledge of the rate of pressure build-up is a necessary requirement when long term missions are being considered.

The pressure leg in Figure 2-1 contains a step indicating the determination of the pressure build-up rate. This step is detailed further in Figure 2-2. A necessary part of the determination is the selection of the proper gas measurement technique. Depending on the type of gas expected, various measurement techniques are available. For oxygen and hydrogen gases, very sensitive measurement techniques are available, the Hersh Cell and the Palladium Foil Analyzer, respectively [1-1]. The situation for other common gases such as  $N_2$  and  $NH_3$  is not so good. Common pressure measuring techniques such as the bourdon gage or strain gage can be used; however, the sensitivity is not truly adequate to detect small gas evolution in short periods. Quite possibly mass spectral analysis of the gas products would yield values for trace amounts of these gases. The spoon gage shows promise of being a very sensitive tool for monitoring pressure rise. This type of pressure gage, as developed by Naval Weapons Center, China Lake [2-1], employs a fine glass lever arm which is attached to a mirror. The mirror is used to reflect a light beam and, since the mirror movement responds to pressure change, the light beam is correspondingly moved by the pressure change. The lever arm of the light beam can produce a large mechanical advantage and thus show very small changes in pressure. It is thus similar in operation to a sensitive mirror galvanometer. The spoon gage apparatus requires calibration before use and the inherent accuracy of the system depends on the construction of the glass apparatus. It has the disadvantage that it is very delicate.

Once the type of measuring system has been chosen, the detailed immersion test can be planned as shown in Figure 2-2 and expanded in Figure 2-3. The detailed immersion test is general and applies to metal build-up and surface degradation as well. Discussion of this part of the method is found in Section 2.2.



# DETERMINE RATE OF PRESSURE BUILDUP

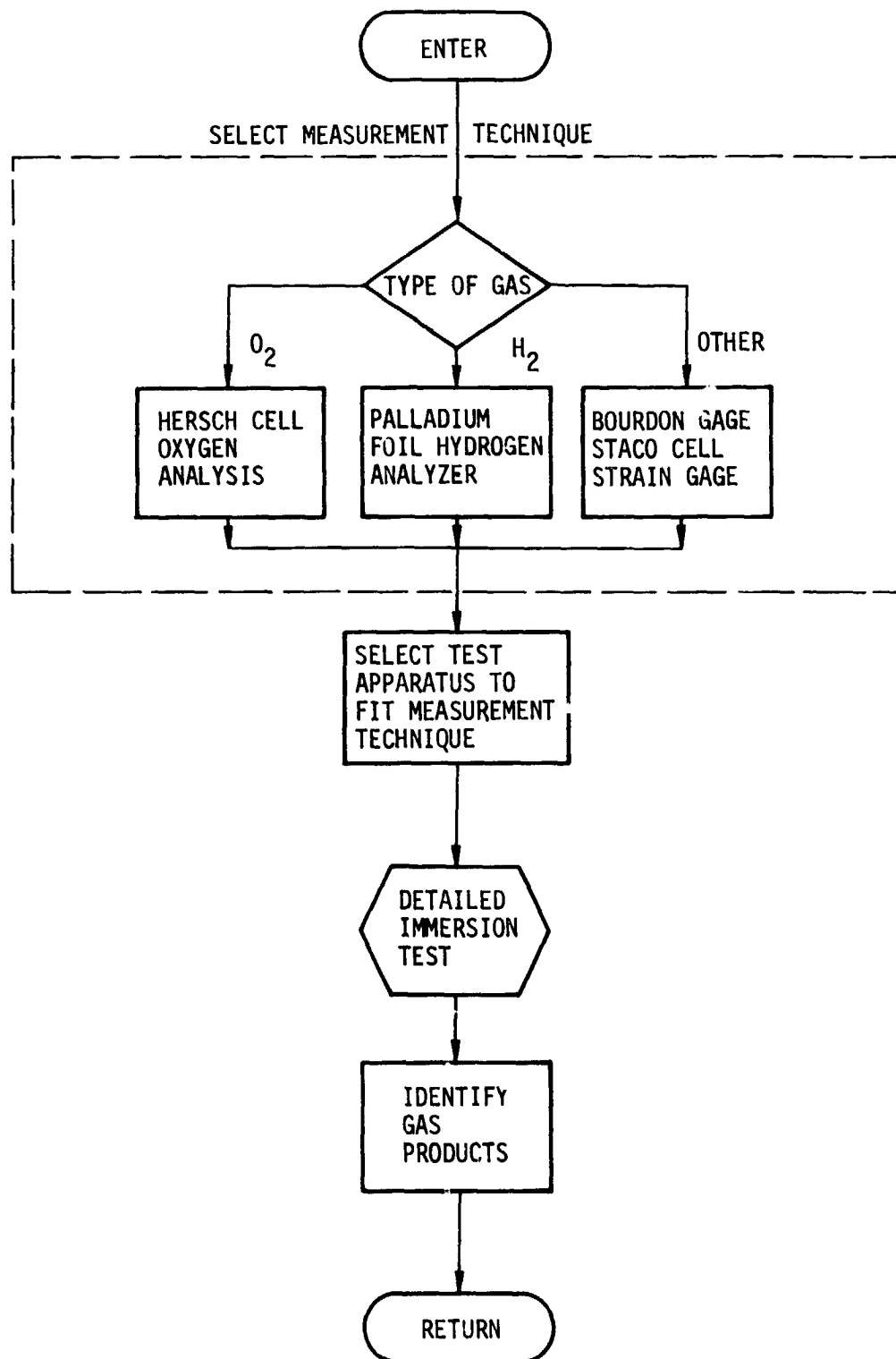
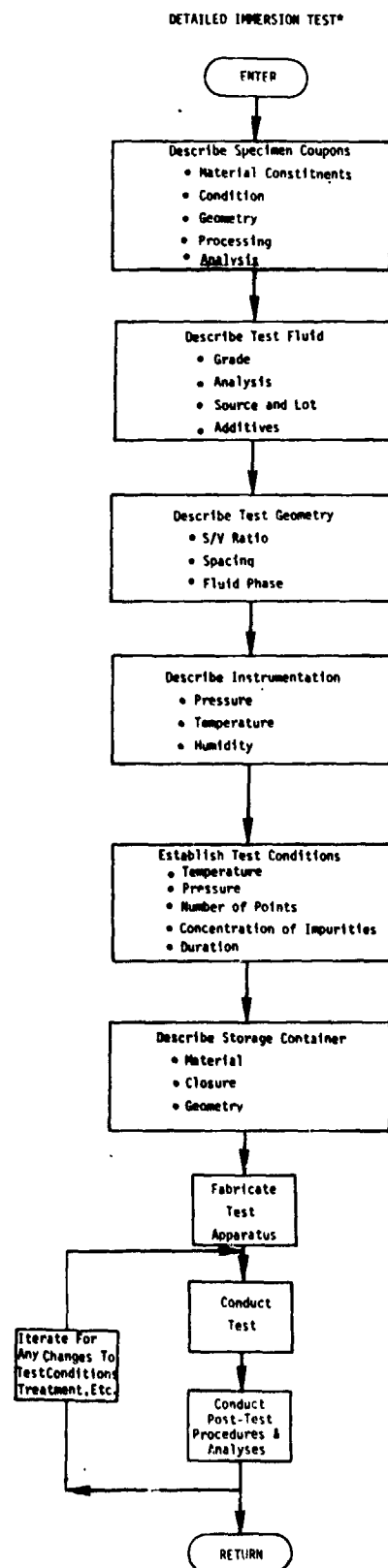


FIGURE 2-2: DETERMINATION OF THE RATE OF PRESSURE RISE



\* Conduct in accordance with ICRPG "Recommended Practices for Static Immersion Testing of Materials..." where applicable.

FIGURE 2-3: DETAILED IMMERSION TEST

The results of the immersion test will yield data concerning the time dependence of gas generation and, presumably, the identity of the gas products. The task then is to develop a rate law describing the reaction that is consistent with the data. The details of establishing the kinetic rate law are given in Section 2.3. If there is no pressure rise, this step is omitted and attention is directed to the other legs.

#### 2.1.2 Determining the Rate of Metal Build-up in the Propellant

Interaction between liquid propellants and metal materials results in certain concentrations of those metals appearing in the propellant. This occurs to a greater or lesser extent depending upon the propellant type and the material, but the fact that this does occur in every case makes it important in monitoring the rate of interaction between propellant and material. The extent of interaction also becomes an important criterion in the judgement of the serviceability of the pair for long-term use.

Since even propellant - material pairs deemed compatible interact, albeit subtly, to some extent, it should be possible to measure that degree of interaction provided that a measuring technique sensitive enough is available. Armed with the degree of interaction for a given period of time, it should also be possible to predict with accuracy the time when the interaction will reach significant proportions.

With these thoughts in mind, we set forth to measure the rate of metal build-up in the liquid propellant with the most sensitive techniques presently available. This procedure is outlined in Figure 2-4.

The type alloy under investigation largely determines the measurement technique to be used. While the radioactive tracer technique is perhaps the most powerful technique to use, not all alloys can be effectively studied with this technique. In practice, the alloy should contain as one of the major constituents, an element which can be readily activated and whose radioisotope has a decay half-life no shorter than approximately the length

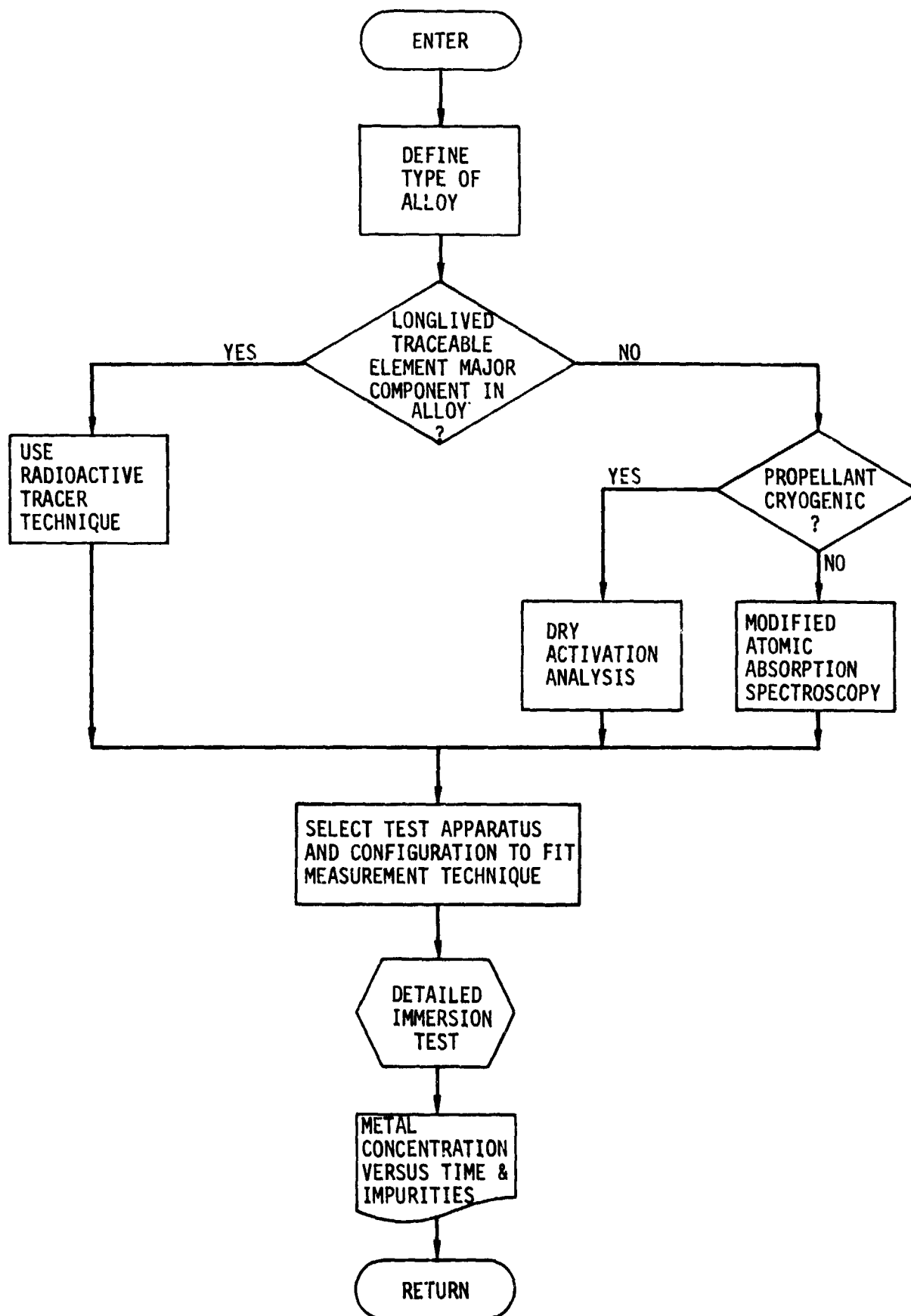


FIGURE 2-4: DETERMINATION OF RATE OF METAL BUILDUP IN PROPELLANT

of the proposed test duration. As a minimum, the radioisotope should have a half-life no shorter than about twelve hours. This rules out elements such as aluminum, titanium, vanadium, magnesium, and silicon. Excellent elements which can be used as tracers include: iron, chromium, zinc, zirconium, cobalt, molybdenum, and many others.

As Figure 2-4 indicates, the radiotracer technique is chosen only if a suitable isotope is available. If not, other methods can be used but at the expense of system complexity and experimental difficulty. In particular this means that, while the propellant - material pair can be studied as a function of time with one test setup and sample using the radio-tracer technique, a test setup and sample for each time point in the investigation must be used for other methods.

If the propellant is not cryogenic, atomic absorption spectroscopy with a graphite furnace is the simple sensitive technique to use. If the propellant is cryogenic, the best procedure to use is the dry activation analysis wherein the residue remaining after propellant evaporation is analyzed by neutron activation analysis. This latter procedure could also utilize atomic absorption spectroscopy but would involve the additional step of dissolving the residue in a suitable solvent. Where simplicity and freedom from error are sought, additional steps such as these are to be avoided. These techniques and others are discussed in detail in Section 3.0.

The particular measurement system chosen will in general determine the type of apparatus to be used in the test program. Selection of materials to be used in the program are also made at this time since they, too, have a bearing on the techniques used.

As in the pressure leg, the detailed immersion test (Figure 2-3) follows these decisions and selections.

The results of the detailed immersion test are used to develop a kinetic rate law describing the rate of metal build-up in the propellant.

### 2.1.3 Determination of the Rate of Surface Degradation

Coupled to the rate of metal build-up in the propellant is the rate of surface degradation of the material. The occurrence of the one usually indicates the presence of the other.

Surface degradation may occur as uniform etching of material, as the development of pin holes or pits, or as the deterioration of a surface film. What effect this surface degradation has on the propulsion system performance depends on the application of the material. For a propellant tank, minute surface pitting would be inconsequential whereas for a transducer with a 1-mil metal diaphragm, surface pitting or pin holes could be catastrophic. Therefore, the rate at which surface degradations take place is an important consideration in the choice of materials.

The procedure utilized for determining this rate is shown in Figure 2-5. Certainly this is not the only procedure that can be used to determine surface degradation; it is a workable one. The procedure can be somewhat complex, depending on the degree of interaction observed.

If there are gross changes observed as a result of the preliminary exposure test, these can be studied by conventional methods and this would preclude any need for the sensitive techniques outlined here.

The absence of gross changes indicates the need to investigate the system further and thus the detailed immersion test is initiated. The study is divided into two parts depending on the formation, or no formation, of a tenacious surface layer of reaction products.

The formation and growth of surface layers is a well investigated subject and it is known that there are various mechanisms of growth that are followed. Some of these mechanisms are: diffusion controlled (parabolic) growth, linear film growth, and logarithmic film growth. Techniques used to measure film thickness include weight gain, polarized light reflection (ellipsometry), and multiple-beam interferometry. Once the time dependence

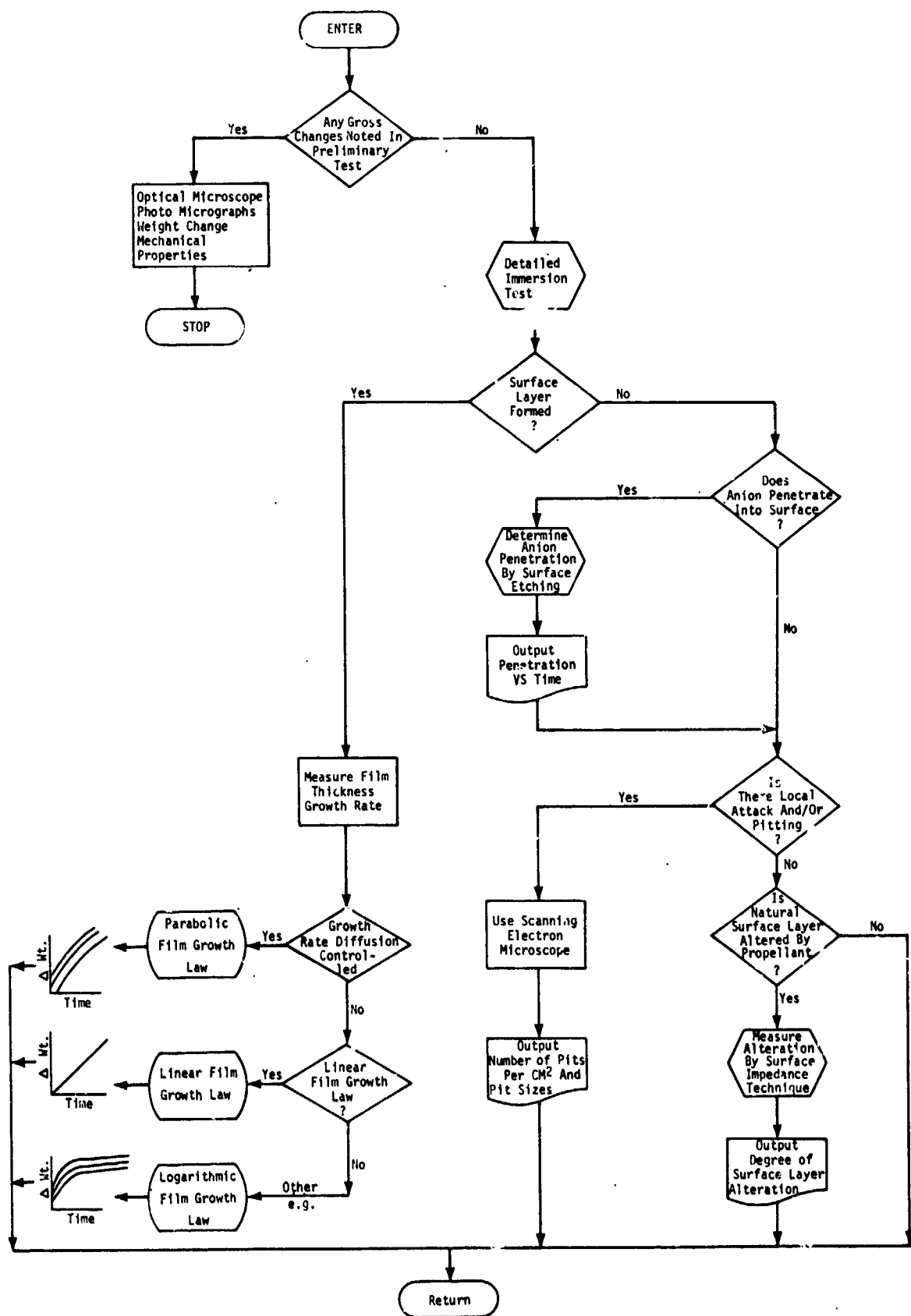


FIGURE 2-5: DETERMINATION OF THE RATE OF SURFACE DEGRADATION

of the film thickness is established the mechanism of film growth can be ascertained and a rate law describing that mechanism can be developed.

For cases wherein no surface layer is formed (or the layer is soluble in the liquid propellant), a separate analysis path is shown. Several possible reactions can occur between the propellant and the material surface. The types of interaction shown in Figure 2-5 are not necessarily meant to include all possible types of interaction but represent typical interaction that would be expected and the approach taken to quantify them.

It is quite possible that, instead of forming a surface layer, the propellant penetrates into the surface in the form of the anion. While this may not be measureable by conventional methods such as the electron microprobe which detects elements only on the surface, it would be possible to establish the amount and depth of penetration by selectively etching the surface of the exposed material and analyzing the etchant for the propellant anion. This technique, shown in Figure 2-6 would be used to develop the penetration depth versus time of exposure to the propellant. The penetration depth could then be correlated to material integrity and strength.

If there is localized attack or pitting of the material surface, the degree of attack can be determined with aid of the scanning electron microscope (SEM). This attack can be quantified as the number of pits per square centimeter and as the size and depth of the pits. This pitting can also be related to the rate of metal build-up in the propellant. Whereas pitting of the surface generally guarantees the presence of metals in the propellant, the reverse is not necessarily true.

It may also be possible that the natural surface film on a material (e.g., aluminum oxide) can be attacked by the propellant and altered in such a way that deleterious effects on the base metal ensue.

Alteration of the natural surface can be conveniently measured using the surface impedance as shown in Figure 2-7. This technique and its applications are discussed in detail in Section 5.0. The degree



DETERMINE ANION RENETRATION BY SURFACE ETCHING

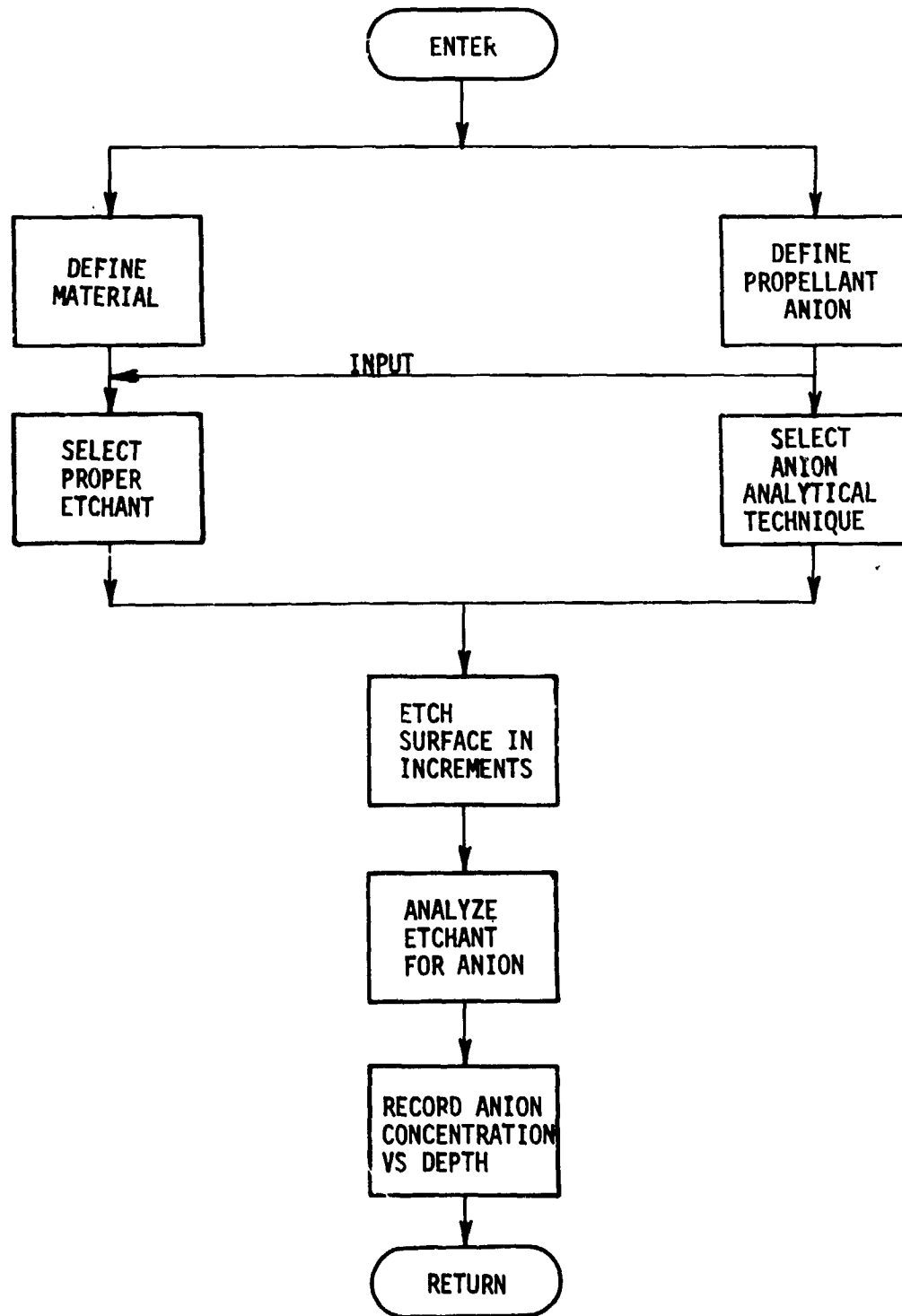


FIGURE 2-6: ANION PENETRATION BY SURFACE ETCHING

MEASURE SURFACE ALTERATION BY SURFACE IMPEDANCE

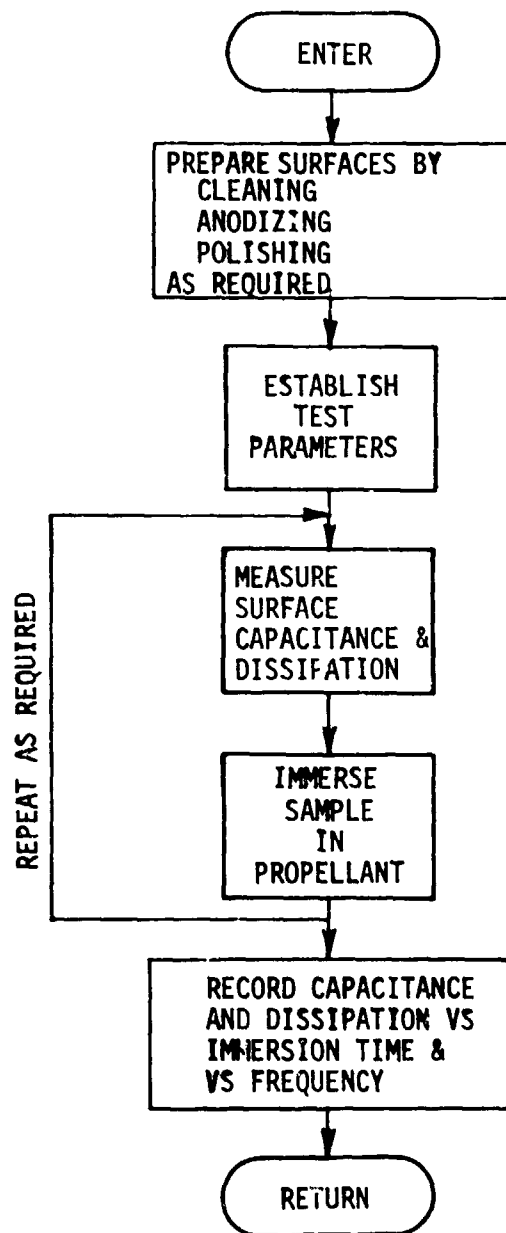


FIGURE 2-7: MEASURE SURFACE ALTERATION BY SURFACE IMPEDANCE

of impedance change versus time is related to alteration of the surface layer and can be used to assess the compatibility of the material-propellant pair.

#### 2.1.4 Completion of the Method

Once the kinetic rate expressions for the interaction of the propellant with the material are known, the expected mission conditions such as temperature and pressure and the expected propellant impurities can be input to the rate expressions. Since the rate of interaction is dependent on time, the selected time can be input and the predicted rate is then defined. This completes the prediction method as shown in the lower part of Figure 2-1.

#### 2.2 DETAILED IMMERSION TEST

The detailed immersion testing procedure shown in Figure 2-3 contains the major elements required to obtain the maximum amount of information about the interaction of propellants and materials in the system defined in Figure 2-1. The objective of the detailed immersion test is to completely describe the various interactions between the liquid propellant and the material in question. These data are used to establish functional relationships between variables, not just single point values.

The preparation and conduct of the detailed immersion test is extremely important and must be carefully controlled and documented if meaningful results are to be obtained. To insure that all possible interactions, variables, and events are considered, a matrix check chart such as the one shown in Figure 2-8 is helpful. These same cautions are outlined rather well in the JANNAF Liquid Propellant Test Methods - Test 726 (LPTM) [2-2] reproduced in part in Appendix A. The terms used in this work are compatible with those given in the JANNAF LPTM and, in general, the procedures used are also those recommended therein. The section in the LPTM on Static Immersion, while as yet incomplete, was used as a model for this work and the detailed immersion test here should be conducted in accordance with those recommendations where applicable.



### 2.2.1 Selection of the Measurement Technique

One of the first items that must be established is the measurement system to be used. This is necessary because of the impact that the measurement technique has upon the other facets of the test plan. For example, the use of the radioactive tracer technique places definite constraints on the geometric configuration of the container for shielding reasons. It may also impose constraints upon the test duration and it definitely places size or weight limitations on the specimen. Other measurement techniques would have their own set of characteristic requirements.

The effect of post-test measurement techniques is somewhat less although they can not be ignored. The dry activation analysis technique, for example, places stringent constraints on the container material used. It must be free of elements being sought or other interfering elements. It must withstand relatively high temperatures during the activation process.

These constraints must not only be known before the remainder of the test plan is developed but may also play an important part in the selection of the measurement technique.

### 2.2.2 Material Specimens

A complete description of the material specimens will include:

Material constituents

Condition, i.e., hardness, surface condition, heat treat

Geometry, i.e., thickness, length, width, weight

Processing, i.e., fabrication, cleaning, passivation

Required number

Analysis

In short, the complete description includes any and all information available about the material and its history.

### 2.2.3 Test Fluid

The description of the test fluid would include:

Grade or MIL Standard

Source and lot number

## Analysis

- assay
- impurities
- additives
- contaminants

### 2.2.4 Specimen - Fluid - Container Configuration

Considerations for Test Geometry are:

Ratio of specimen surface area to fluid liquid volume

Ratio of specimen surface area to fluid gas volume

Spacing between specimens and between specimen and container

Electrical resistance paths

The surface area to volume ratios may be chosen to equal those in a specific application or may be increased to enhance the measurement of a reaction rate. Minimum spacing between specimens is required to insure that there will be no interaction between different types of materials. For the case in which the effect of the material on the propellant is sought, there can be only one material per container. Where there is a possibility of the container material interacting with the specimen, a minimum spacing is required also and certainly no low electrical resistance paths should exist between any specimen or specimen-wall.

### 2.2.5 Storage Container Design

The design of the test storage container must be considered very carefully in light of all interacting aspects such as test measurement method, type of fluid, test environment, etc.. In some cases the container is constructed of the material being studied. The configuration and size of the container is relatively unimportant but must be fully defined. Other container items which must be described are the closure, tubing connections, seal-offs, and any flexures.

### 2.2.6 Instrumentation

Internal Pressure - There are essentially three types of pressure measuring devices in use: external strain gauges, Staco cells, and all metal Bourdon gauges. The type of measuring system chosen will depend on

numerous factors such as cost, fluid type, additives if any, and degree of sensitivity required.

Internal Temperature - Monitoring of internal temperature, if required, can be accomplished by means of thermocouple or thermistor wells. Containers stored in temperature controlled ovens or in liquid baths do not require internal temperature monitoring.

External Pressure, Temperature and Humidity - In cases where these environmental conditions play a role, it is recommended that the procedures outlined in the JANNAF handbook be followed.

#### 2.2.7 Test Conditions

A complete definition of test conditions will include the temperatures, pressures, concentrations of impurities, duration, and number data points.

#### 2.2.8 Fabrication and Installation of Test System

Once the test plan is described, fabrication of the apparatus, container, and specimens may be accomplished.

#### 2.2.9 Conducting the Test

The conduct of the test program should follow established test procedures and safe operating practices. Items that are included in the testing procedure are:

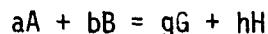
- Specimen mounting
- Installation of the mounted array
- Inspection
- Container sealing
- Leak checking
- Calibration
- Fluid fill
- Storage monitoring
- In-situ measurements
- Test Termination

### 2.2.10 Post-Test Measurements

There will be a wide variety of post-test measurements which depend upon the type of test conducted and the particular material-propellant pair tested. Some of these measurements have been discussed previously in Section 2.1 and are discussed fully in Reference 2-2. Upon completion of the post-test procedures and analyses, the test conditions are changed as required and the testing is continued.

### 2.3 ESTABLISHING THE KINETIC RATE EXPRESSION

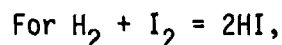
Figure 2-9 shows pictorially the method used to develop the kinetic rate expression from the data generated during the detailed immersion tests. First, all data must be collected and displayed so that trends and dependence on the test variables can be clearly visualized. The problem then becomes one of determining the order of the reaction with respect to all the participants. In the general reaction with stoichiometric equation



the rate may be expressed by

$$-d[A]/dt, -d[B]/dt, d[G]/dt, \text{ or } d[H]/dt$$

where  $t$  is time and brackets mean concentration. The reaction rate at a given temperature is a function of the concentrations of some or all of the various components of the system, but usually only the reactants. The functional relation between rate of reaction and the concentrations is called a rate expression. In general it is not possible to predict the rate expression for a given reaction by just knowing the stoichiometric equation. An example of a rate expression is:



$$\frac{d[HI]}{dt} = k [H_2][I_2]$$

where  $k$  is the reaction rate constant. Very few rate expressions are this simple. Some reactions can be represented with a rate expression of the form:

$$-dc_1/dt = k c_1^{n_1} c_2^{n_2} c_3^{n_3}$$



## ESTABLISH KINETIC RATE EXPRESSION

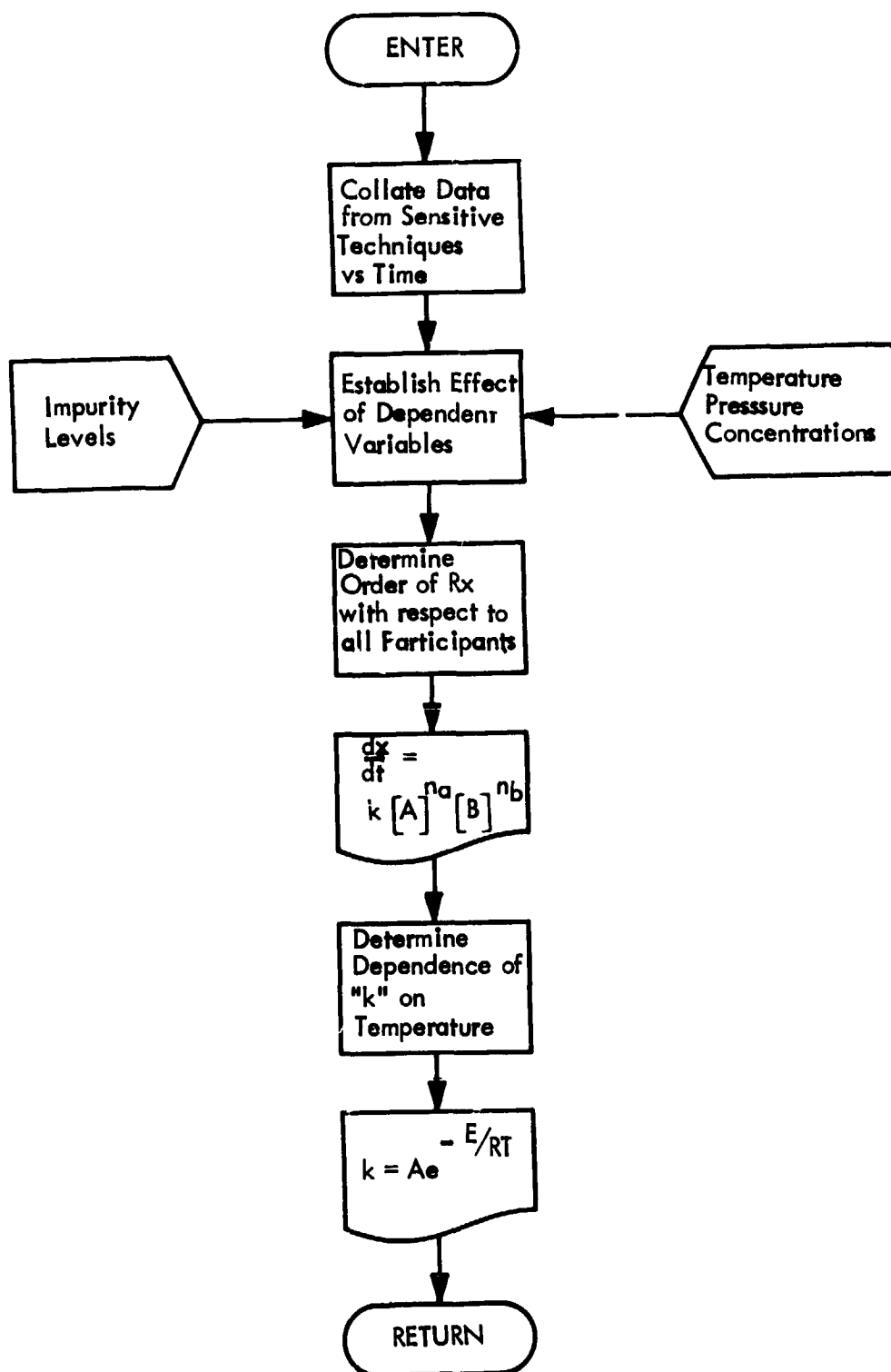


FIGURE 2-9: ESTABLISHING THE KINETIC RATE EXPRESSION

For this restricted type of rate expression there is defined the concept of "order of reaction,  $n$ ," where  $n = n_1 + n_2 + n_3 + \dots$ , the sum of all the exponents of the concentrations. Each individual exponent is called "the order with respect to that component." For example in the reaction above for hydrogen iodide, the reaction is second-order, but the order with respect to each reactant separately is one. Occasionally the exponents may be fractional or even negative, depending on the complexity of the reaction. It should be emphasized that these expressions are empirical in nature.

The rate of reaction is not usually obtained directly from experimental data, but instead a concentration or some other variable is measured as a function of time. In a plot of concentration versus time, the rate at any time is equal to the slope of the curve. Since the concentrations are usually observed, the integrated form of the rate expression is more convenient to work with. The first-order reaction represented by the rate expression

$$-\frac{dc}{dt} = k c$$

can be readily integrated to yield

$$\ln (c/c_0) = kt$$

or  $\ln c = \ln c_0 + kt$

To test experimental data for a first-order reaction, the  $\ln c$  or  $\log_{10} c$  is plotted versus time and should be linear with a slope of  $k$  or  $k/2.303$ , respectively. See Figure 2-10(a).

For a second-order reaction,

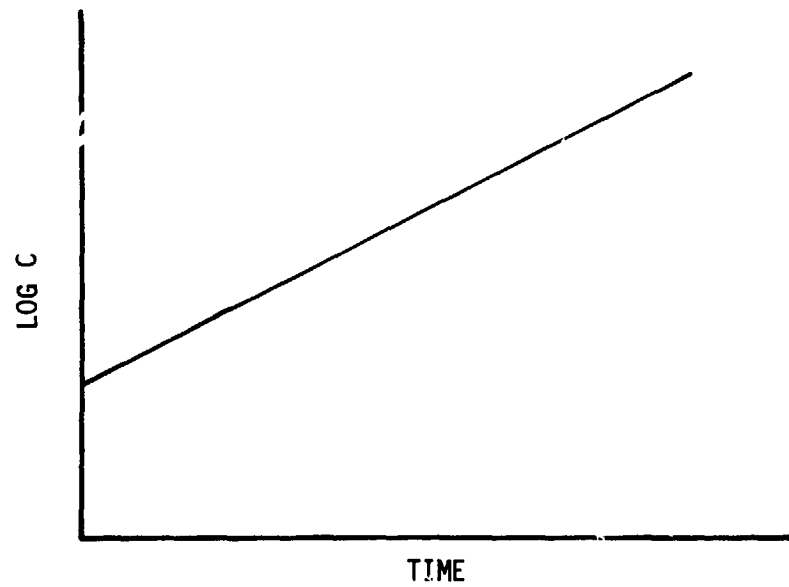
$$\frac{dc}{dt} = k c^2$$

the integration yields

$$\frac{1}{c_0} - \frac{1}{c} = kt$$

Again, according to this expression, a plot of  $1/c$  versus time should be linear, and with a slope equal to  $k$ . See Figure 2-10(b). Other rate expressions can be similarly integrated. The second-order reaction whose

(a) FIRST-ORDER REACTION



(b) SECOND-ORDER REACTION

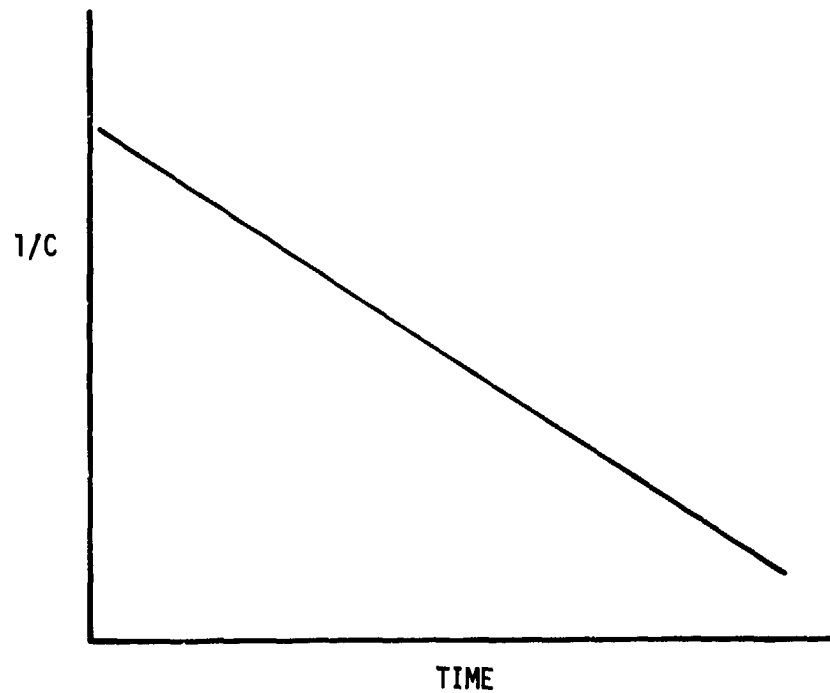
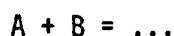


FIGURE 2-10: LINEAR PLOTS FOR FIRST AND SECOND-ORDER REACTIONS

stoichiometry is



and whose rate expression is

$$\frac{-dA}{dt} = k AB$$

can be integrated to give

$$\frac{1}{B_0 - A_0} \ln \frac{A_0 B}{B_0 A} = kt$$

where  $A_0$  and  $B_0$  are initial concentrations of A and B. It is evident that data may be tested by plotting  $\log (B/A)$  versus time yielding a linear plot if the expression is valid.

Although kinetic rate expressions are usually written in terms of the rate of decrease of one of the reactants, they sometimes are more conveniently written in terms of the rate of buildup of one of the products. Consider the reaction  $A + B = Y + Z$  and rate expressions that are zero, first, second, and third order with respect to A. The various equivalent expressions are shown as follows, where  $A_0$  is the initial concentration of the reactant A. Note that the decrease in concentration of the reactant

Order of Reaction With Respect to A	Rate Expressions in Terms of the Decrease in Concentration of Reactant A	Rate Expressions in Terms of the Increase in Concentration of Product Y
zero	$-\frac{dA}{dt} = k_0$	$\frac{dY}{dt} = k_0$
first	$-\frac{dA}{dt} = k_1 A$	$\frac{dY}{dt} = k_1 [A_0 - Y]$
second	$-\frac{dA}{dt} = k_2 A^2$	$\frac{dY}{dt} = k_2 [A_0 - Y]^2$
third	$-\frac{dA}{dt} = k_3 A^3$	$\frac{dY}{dt} = k_3 [A_0 - Y]^3$

A is exactly equal to the increase in concentration of the product Y. Also, note that in the early stages of the reaction when Y is much smaller than  $A_0$ , the value of  $dY/dt$  for the first, second, and third-order reactions will in effect equal a constant. These reaction rates in their initial stages are therefore termed pseudo-zero-order.

Figure 2-11 shows typical shapes of curves for various types of reactions. Curve (a), the autocatalytic reaction, was drawn under the assumption that one of the products of the hypothetical reaction acts as a catalyst to increase the rate of reaction. As more product is formed with time, the reaction rate continues to increase.

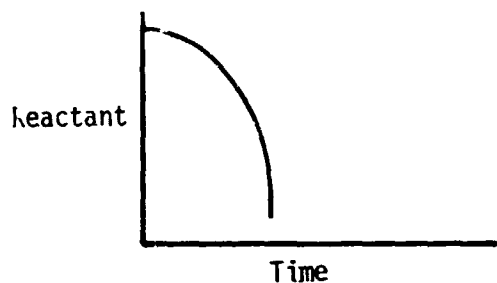
It is evident that the development of the rate expression is a trial-and-error process; however, information about the mechanism of the reaction can be a great aid in this development. Conversely, knowledge of the rate expression can shed much light on the mechanism of the reaction. A complete treatment of this subject is beyond the scope of this work and the reader is referred to any appropriate reference on chemical kinetics for additional information.

Kinetic rate expressions are not limited to description by concentrations of reactants. In general, procedures for determining kinetics may be divided into two categories, chemical and physical. Chemical analysis implies a direct determination of the concentration of one or more of the reactants or products. Physical methods of analysis are also utilized and have the advantage of being much more convenient than chemical methods. A physical method is one which measures some physical property of the reaction mixture, which changes as the reaction proceeds. Common physical methods are pressure measurement, volume change, colorimetry, spectrophotometry, conductivity, and mass spectrometry. Theoretically, any property which changes with time could be used to follow the course of a reaction, it is only necessary that the change be correlatable to the reaction process.

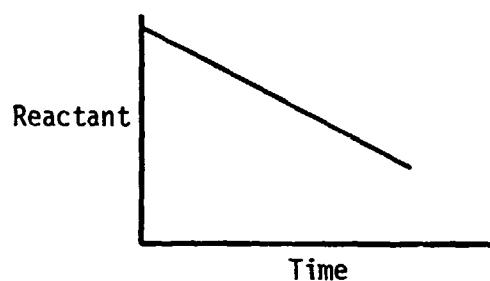
It is well established that most chemical reactions are not constant, but rather are a function of the temperature. The dependence of the reaction rate constant,  $k$ , upon the temperature can be established through experiments at temperatures varied within reasonable limits. Various

Curve Shapes Showing Decrease of Reactant as a Function of Time

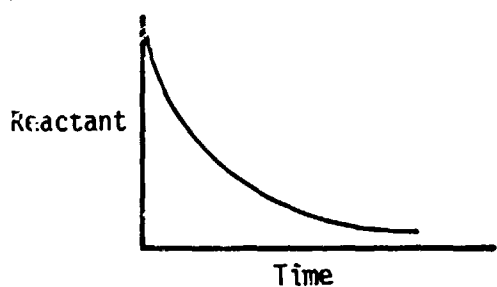
(a) Autocatalytic



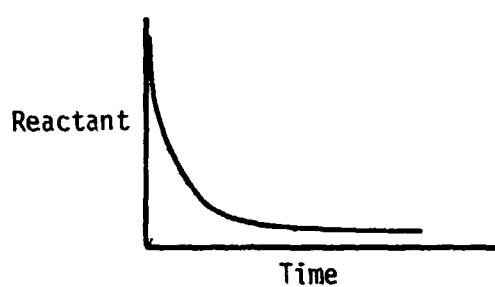
(b) Zero Order



(c) First Order

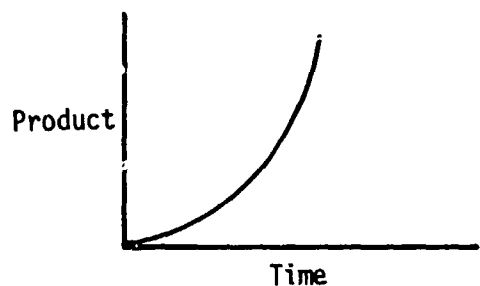


(c) Second Order

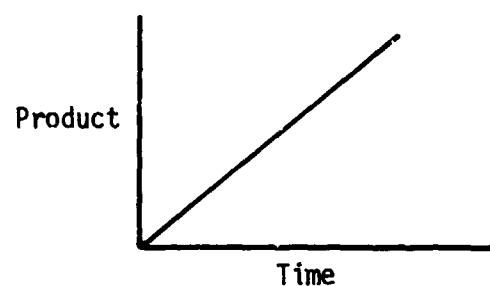


Curve Shapes Showing Increase of Product as a Function of Time

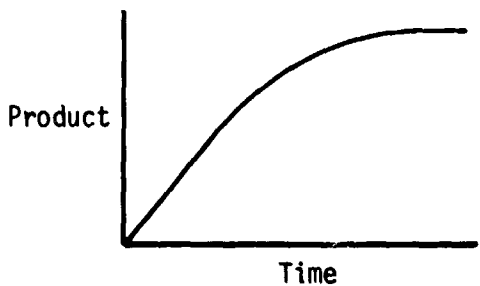
(a) Autocatalytic



(b) Zero Order



(c) First Order



(d) Second Order

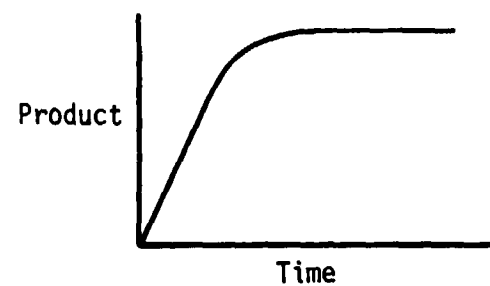


FIGURE 2-11: CURVE SHAPES FOR VARIOUS REACTION RATES

types of temperature dependence are observed experimentally but the type shown in Figure 2-12 is the most common, and above a certain temperature the rate increase tends to level off. This may be called the Arrhenius temperature dependence. It is usually found that a plot of  $\log k$  versus  $1/T$  is nearly linear, with a negative slope. This is in concert with the Arrhenius equation

$$k = Ze^{-E_a/RT}$$

where  $E_a$  is called the Arrhenius activation energy and it is assumed  $E_a$  is constant with respect to temperature.

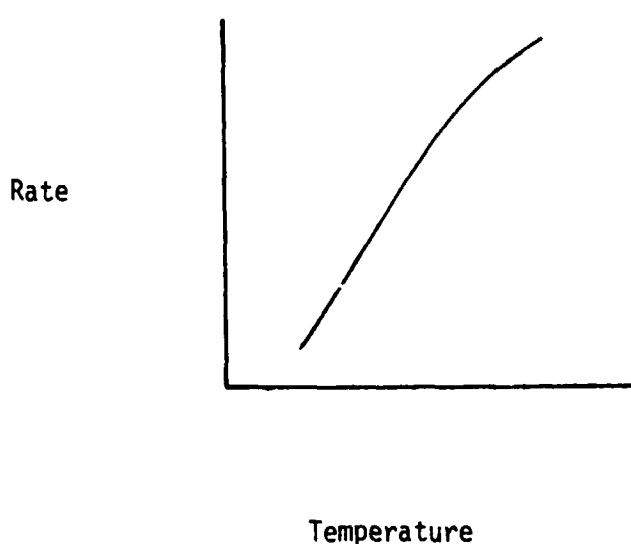


FIGURE 2-12: DEPENDENCE OF REACTION RATE ON TEMPERATURE

#### 2.4 USING THE PREDICTION METHOD

The use of the prediction method may be broken into two categories: (1) use with well-defined systems and (2) use with other systems. A well-defined system can be described as one in which all of the scientifically interesting facts concerning the system are known. That is, the mechanism of the reaction is known, the kinetic rate expression is known, and the temperature dependence of the reaction rate constant is known. Other systems can be described as ones in which one or more of the above items are not known.

#### 2.4.1 The Well-Defined System

The use of the prediction method for a material-propellant system which has been well-defined can proceed in a straightforward manner. The concentrations of known participants in the kinetic rate expression(s) can be established through analysis of the propellant. The temperature anticipated during service can be determined through engineering studies. These facts allow the direct calculation of the degree of interaction between propellant and material during service.

#### 2.4.2 Other Systems

The fact that certain elements of the description of the propellant-material system are not defined does not necessarily mean that a prediction cannot be made. It may mean, however, that limitations or qualifications must be placed on the prediction.

Let us consider some situations in which a prediction can be made. Assume that the preliminary exposure test indicates that the system is satisfactory for further study. Furthermore, let us assume that the detailed immersion test has indicated no pressure buildup, no metal buildup and no surface degradation. Quite obviously, with this lack of information it is not possible to develop a kinetic rate expression defining the interaction between propellant and material. Nevertheless, we can make a prediction. Our prediction is, within the limitations of the detection sensitivity of the methods used, that there will be no deleterious interaction between the propellant and material for an unlimited time.

Now, let us consider a system in which the detailed immersion test indicates metal buildup at relatively high concentrations of propellant impurity but no metal buildup at low concentrations of impurity. Assume also, that the metal buildup is of such a low value that the measurements are at or near the limit of detection of the technique used, thereby causing sufficient scatter in the data to render it impossible to determine a



kinetic rate expression. In this situation, a prediction can be made by utilizing those data points that correspond to the highest rate of reaction and calculating a maximum, or upper limit, to the corrosion rate. Thus, the "worst possible case" is used to generate a kinetics expression. This assumed rate expression is then applied to the propellant-component system under investigation. If the extent of corrosion for the desired time period is found to be below the previously established acceptable limits, then the system is deemed compatible.

### 3.0 DESCRIPTION OF ADVANCED TECHNIQUES

Part of the basic foundation of the prediction method is an array of sensitive measurement techniques which can be applied to analysis of a given material-propellant combination for a short test period and which can produce reliable data on the interaction rates. A number of applicable techniques have been discussed previously [1-1]. It is the intent of this section to discuss those techniques which were used in the laboratory verification of the prediction method.

#### 3.1 NEUTRON ACTIVATION ANALYSIS

##### 3.1.1 Theory

Stable isotopes, when irradiated by neutrons, can undergo a nuclear transformation to produce a radioactive nuclide. Qualitative and quantitative conclusions can be made of the elemental composition and amount of the original sample before irradiation by characterizing the emanations of the radionuclide with radiation detection equipment. This is the basic principle of activation analysis.

While stable isotopes can undergo a variety of nuclear transformations, the reaction most widely used in activation analysis is the neutron-gamma ( $n, \gamma$ ) reaction. Examples of such reactions are shown in Eq. 3.1 and 3.2



The ( $n, \gamma$ ) reaction is primarily a thermal-neutron reaction which can be produced by a variety of neutron sources. The nuclear reactor also possesses fast neutrons which can produce neutron-proton ( $n, p$ ) reactions and neutron-alpha particle ( $n, \alpha$ ) reactions. In a ( $n, p$ ) reaction, the nucleus releases a proton and the atomic number is reduced by 1 forming a different element.



In the ( $n, \alpha$ ) reaction, an  $\alpha$  particle is emitted and the atomic number is reduced by 2 as



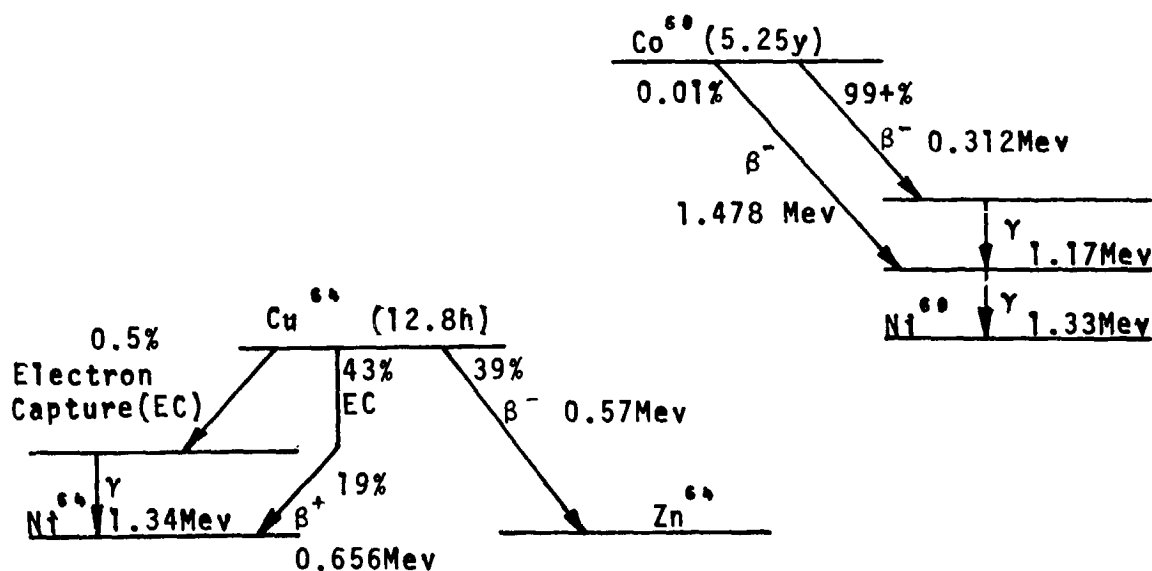
The induced radioactivity in irradiated samples decreases exponentially with time and varies with each individual isotope. The length of time required for this activity to decrease by one half is referred to as the half-life ( $T_{1/2}$ ). This radioactive decay can be expressed by the equation

$$A_t = A_0 \exp (-0.693 t/T_{1/2}) \quad (3.5)$$

where  
 $A_0$  = initial radioactivity  
 $A_t$  = radioactivity remaining after time  $t$   
 $T_{1/2}$  = the half-life of the radioisotope

It is the decay of the radioactivity and its associated emanations that are used in neutron activation analysis. The decay is usually accompanied by emission of subatomic particles and/or electromagnetic radiation. The emission that is of interest in this work is the photon emission ( $\gamma$ ).

A convenient method for graphically illustrating the modes of decay of a radioisotope is the decay scheme. Two examples are shown below



The induced activity,  $A_0$ , in the radioisotope is a function of several variables including the flux of neutrons impinging on the target

nucleus, the target's cross-section for activation by the neutron, and the product half-life. Expressed mathematically the induced radioactivity after irradiation for time  $t$  is

$$A_0 = \phi \sigma f N_0 (1 - e^{-\lambda t}) \quad (3.6)$$

where  $\phi$  = neutron flux,  
 $\sigma$  = target isotope neutron cross-section,  
 $f$  = fractional abundance of target isotope  
 $N_0$  = total number of atoms,  
 $\lambda = \ln 2 / T_{1/2}$

The exponential decay factor in the expression in Eq. 3.6 corrects for decay of induced activity during the activation process.

### 3.1.2 Practical Considerations

In the analysis of a complex sample, the emanations resulting from the activation are separated according to energy and are counted for a pre-determined length of time. This allows both the identity and the amount of product to be established. Appropriate standards are used to correct for variations in geometry and counting efficiency.

The electronic computer is playing an increasingly important role in analysis by neutron activation. The computer is used to sort and store data as it is counted by a gamma spectrometer and a computer is used to reduce and evaluate the data for the researcher. See Figure 3-1.

### 3.1.3 Equipment

Aside from the comparatively vast amount of equipment used to produce the radioactive isotopes, there is a certain amount of equipment that is needed by the analyst to use the neutron activation technique.

The characteristic emanations from the radioisotopes are generally detected by scintillation devices or semiconductor devices depending on the requirements of the analyst. At this time, the crystal detectors used in scintillation devices have the advantage of low cost and higher efficiency,

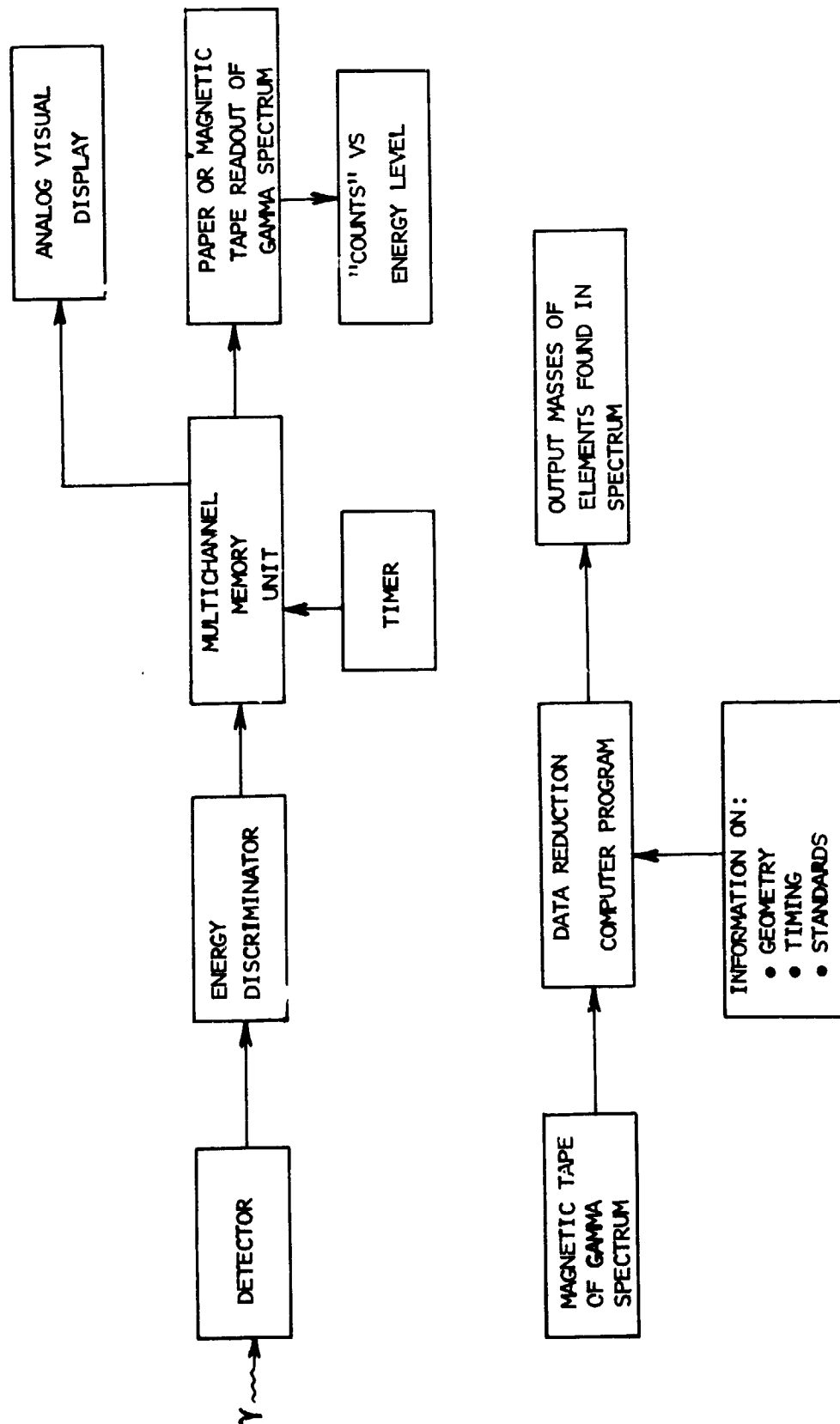


FIGURE 3-1: NEUTRON ACTIVATION ANALYSIS

whereas the semiconductor devices have the advantage of much higher resolution.

Once the electromagnetic radiations have been detected by one of the above devices, the energy level is established by a multichannel analyzer and the number of "counts" received is stored by energy level in a computer memory. As these counts are received they are continuously added in the memory unit until the specified count time is completed. The total number of counts versus energy level are then output via magnetic tape or hard copy. Most analyzers also provide a visual display of the gamma spectrum on an oscilloscope.

The gamma spectrum or the total number of counts in a given energy range is then used to quantify the total mass of the product radioisotope. This can be done by hand calculations but many analysts now utilize the electronic computer to perform this arduous task.

#### 3.1.4 Experimental Procedures of the Dry Activation Analysis Technique

The experimental procedures of the dry activation analysis technique mentioned in Section 2.1.2 and shown in Figure 2-4 differ only slightly from the standard recommended procedures for static immersion testing. The overall procedure is outlined in Figure 3-2. Items that are peculiar to this technique are the choice of the container material, the activation of the propellant residue and associated gamma counting.

The choice of the container has significant importance because of the desirability to activate the residue in the original container. This reduces the possibility of errors arising from the transfer of residue to another container for the purposes of neutron activation. The container material chosen must not have elements in its makeup which when activated will produce radiations which will interfere with the residue analysis.

#### 3.1.5 Detection Sensitivity Limit

The sensitivity of the method is governed by a number of variables. Some of these are associated with laboratory equipment, others are associated with the physical nature of the elements studied.

DRY ACTIVATION ANALYSIS

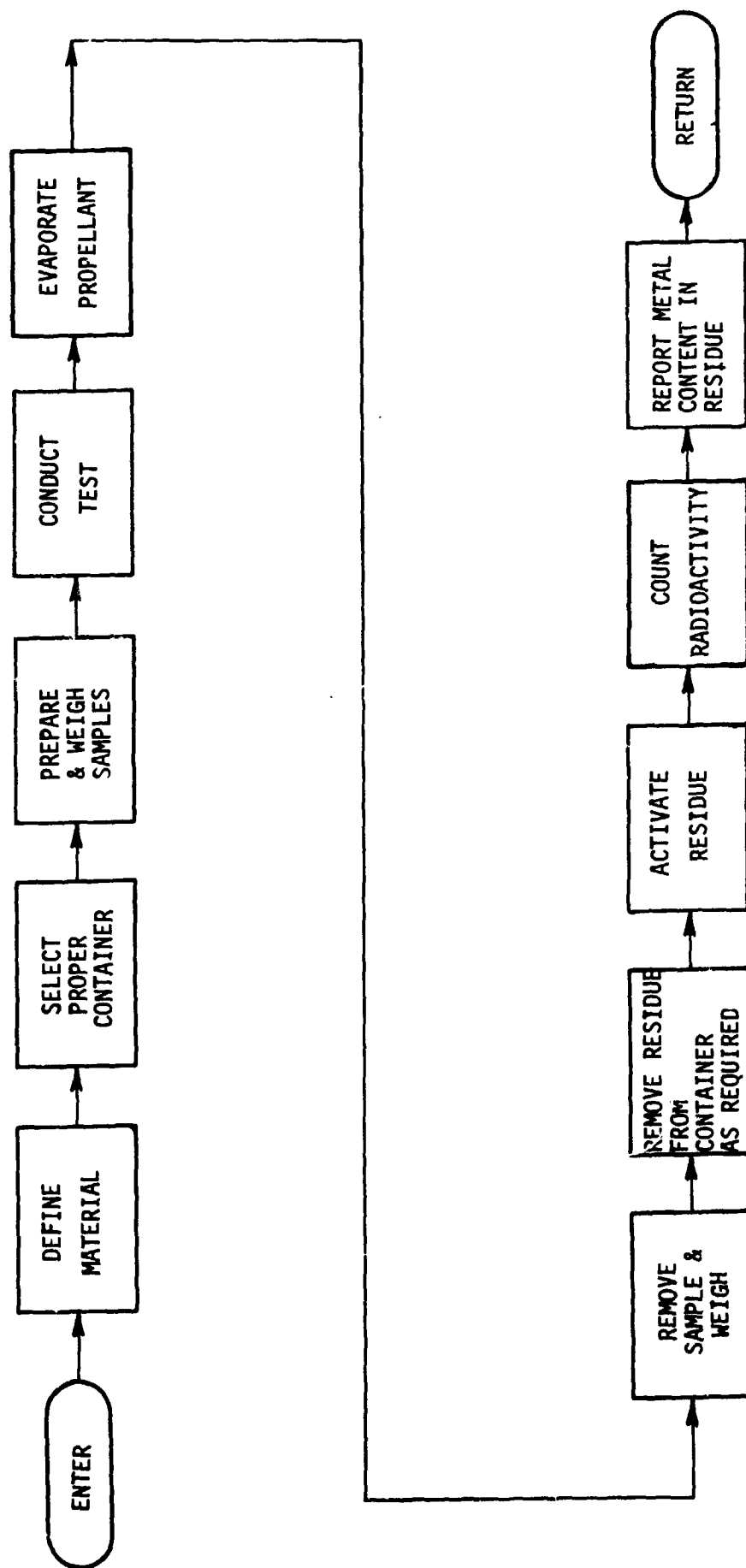


FIGURE 3-2: DRY ACTIVATION ANALYSIS TECHNIQUE

The amount of element of interest can be quantified according to Eq. 3.7

$$\text{mass} = \frac{\text{A.W.}}{\text{AV}} N_0 \quad (3.7)$$

where A.W. = the atomic weight of the element  
 $N_0$  = number of atoms of atomic weight A.W.  
 AV = Avogadro's number

This is related to the mass of the element in the residue by

$$\text{mass} = \frac{\text{A.W.}}{\text{AV}} \left( \frac{N'}{N_0} \right) \quad (3.8)$$

where  $N'$  is the number of radioactive atoms measured and  $N'/N_0$  is ratio of radioactive atoms to total atoms. The quantity  $N'$  is given by

$$N' = \frac{R_N}{\lambda \cdot (\text{detector efficiency}) (\text{number of } \gamma\text{'s per disintegration})} \quad (3.9)$$

where  $R_N$  is the net count rate.

The quantity  $N'$  in the ratio  $N'/N_0$  is also given by the initial induced radioactivity, Eq. 3.6, and also

$$A_0 = dN/dt = \lambda N' \quad (3.10)$$

Rearranging the equation and substituting Eq. 3.6 we get

$$N' = \frac{\phi \sigma f N_0 (1 - e^{-\lambda t})}{\lambda} \quad (3.11)$$

and the ratio  $N'/N_0$  becomes

$$\frac{N'}{N_0} = \frac{\phi \sigma f (1 - e^{-\lambda t})}{\lambda} \quad (3.12)$$

Substituting Eq. 3.9 and 3.12 into Eq. 3.8 we get

$$\text{mass} = \frac{\text{A.W. } R_N}{\text{AV } \phi \sigma f (1 - e^{-\lambda t}) (\text{detector efficien.}) (\frac{\gamma\text{'s}}{\text{disint.}})} \quad (3.13)$$

Thus it becomes apparent that to detect the minimum amount of mass one requires the minimum meaningful count rate, the maximum neutron flux,



the longest practical activation time, and the maximum possible detector efficiency. There are certain quantities that of course can not be changed for a given element but do limit the sensitivity: the neutron cross-section, the fractional abundance and number of gammas or other particles per disintegration.

Using Eq.3.13, a sample calculation for titanium is made. Assume the following information:

$$\begin{aligned} R_N &= 100 \text{ counts per minute} \\ \phi &= 7.1 \times 10^{13} \text{ neutrons/cm}^2/\text{sec} \\ \sigma &= 0.14 \times 10^{-24} \text{ cm}^2 \\ f &= .053 \\ \lambda &= 0.693/5.80 \text{ minutes} \\ t &= 6.0 \text{ minutes} \end{aligned}$$

detector efficiency = .05

number of gammas per disintegration = 1.0

The minimum detectable mass then becomes

$$\begin{aligned} \text{mass} &= \frac{(47.90) (100/60)}{(.602 \times 10^{-24}) (7.1 \times 10^{13}) (.14 \times 10^{-24}) (.053) (1 - e^{-(.693)(5.8)/6.0}) (.05)} \\ &= 1.03 \times 10^{-8} \text{ grams} \end{aligned}$$

This calculation assumes a pure titanium sample and does not consider the interference of other elements possibly present.

### 3.2 RADIOACTIVE TRACER TECHNIQUE

#### 3.2.1 Theory

The theoretical aspects of the radioactive tracer technique are essentially the same as those of the neutron activation analysis technique. The differences between the two techniques are basically found in the practical aspects of applying the radiotracer technique.

#### 3.2.2 Practical Considerations

The radiotracer technique ideally uses one or only a few radioisotopes for an application since this simplifies the bookkeeping and interpretation of results. The material of interest is placed in the nuclear reactor, or other suitable neutron source, for a specified length of time and then the sample is removed and placed in contact with the liquid propellant for predetermined lengths of time.

With the radioactive sample removed from the propellant, the radioactivity transferred to the propellant is determined with a radiation detector. The quantity of radioactivity is correlated to the metals transferred from the sample to the propellant.

#### 3.2.3 Equipment

The equipment required for the gamma counting can be somewhat less complex than that required for the neutron activation analysis. While desirable, a complete gamma spectrum of the radioactivity in the propellant is not necessary since the energy of the radioisotope is established. The detector/counting setup may consist simply of a radiation detector, an energy discriminator (analyzer), a scaler capable of counting pulses output from the analyzer, and an electronic timer capable of stopping the counting at accurately determined intervals.

#### 3.2.4 Experimental Procedure

The details of the experimental procedure for the radioactive tracer technique are outlined in Figure 3-3. The unique aspects of this technique lie in the choosing of the proper radioisotope to monitor during the course of the investigation, the activation of the sample and its associated calculations, and the counting of the transferred radioactivity in the propellant during test.

## RADIOACTIVE TRACER TECHNIQUE

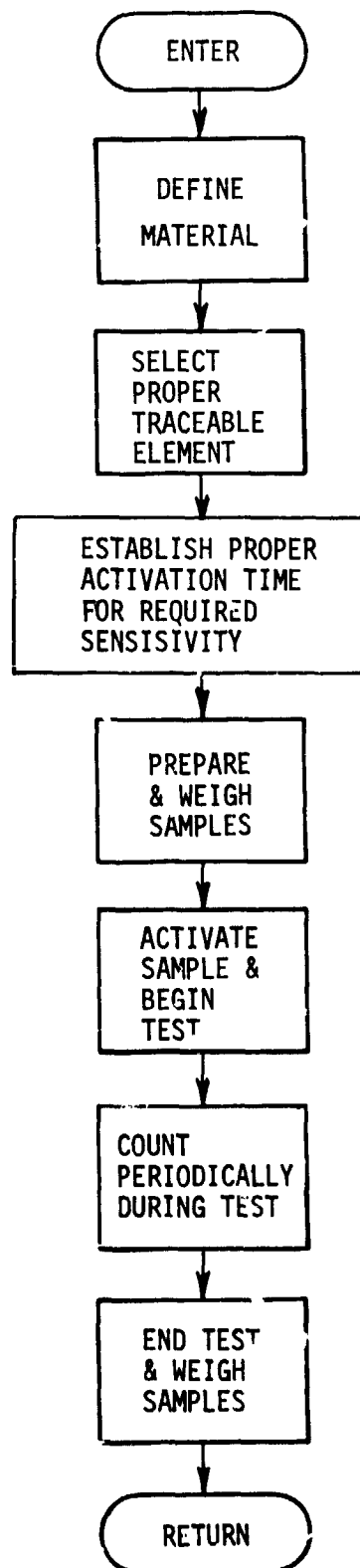


FIGURE 3-3: RADIOACTIVE TRACER EXPERIMENTAL PROCEDURE

The choice of the element that is to be used as the tracer depends mainly on the half-life of the radioisotope. The half-life must be sufficiently long so that the length of the experiment is not severely penalized by the effects of radioactive decay (which translates into a loss in sensitivity) nor must the half-life be so long that the sensitivity of the method is penalized by exorbitantly long activation times required to reach acceptable activity levels. More details concerning the sensitivity of the method are given in Section 3.2.5. This narrows the choice of elements to those with radioisotopes with half-lives of the order of the 10-15 hours up to, say, one year.

The establishment of the proper amount of neutron activation of the tracer is also of some importance for this often governs the financial aspects of the method. As shown in Eq. 3.6, the induced activity is proportional, among other things, to time in the reactor, and time in the reactor is proportional to the cost. The activity is also proportional to the neutron flux in the reactor (or other source), the cross-section of the nucleus, the number of target atoms (this is a function of the concentration of the element in the material of interest and the relative abundance of the isotope in question), and the half-life of the radioisotope produced. All other aspects being equal there is often a trade-off between reactor flux and cost, with higher flux reactors giving more neutrons per dollar. Since the induced activity ultimately determines the sensitivity of the measurement, the time of activation is defined.

### 3.2.5 Detection Sensitivity Limit

The calculation of minimum detectable mass is identical with that discussed in Section 3.1.5. For the radioactive tracer technique, the minimum detectable mass begins to increase the minute the tracer leaves the reactor. As a function of time, the mass given by Eq. 3.13 increases by the factor  $e^{\lambda t}$  where  $t$  is the time since the cessation of the activation process. This means that where  $\lambda$  is comparable to  $t$  that the detection sensitivity changes rapidly during the course of the experiment. Therefore, long-lived radioisotopes are desirable for tracer work.

An example calculation for an isotope of interest (copper - 64) shows the following detection limit (using Eq. 3.13) for an activation time of 2 hours:

$$\begin{aligned} \text{mass}_{\min.} &= \frac{(63.54) (100/60)}{(.602 \times 10^{-24}) (7.1 \times 10^{13}) (4.5 \times 10^{-24}) (.691) (1 - e^{-.1074}) (.05) (.19)} \\ &= \frac{105.9}{.01286 \times 10^{13}} = .823 \times 10^{-9} \text{ grams copper} \end{aligned}$$

Thus, immediately after irradiation, assuming a net count rate of 100 cpm, the detection limit is .8 nanograms. The detection limit at any time  $t$  after irradiation is

$$\text{mass}_{\min.} = .823 e^{-.0537 t} \text{ nanograms.}$$

Note that the minimum detectable mass doubles every half-life or, in the case of copper, every 12.9 hours.

### 3.3 ATOMIC ABSORPTION SPECTROSCOPY WITH GRAPHITE TUBE FURNACE SAMPLER

#### 3.3.1 Theory

The basic principles underlying atomic absorption spectroscopy (AAS) have been known to scientists for over one hundred fifty years, but their application chemical analysis has been developed only within the last two decades [3-1]. The techniques and instrumentation which have evolved are particularly suited to the quantitative determination of the elemental compositions of a wide variety of sample types. One of the more important applications of the method has been in the quantification of trace metals contained in industrial products and wastes.

AAS is based on the principle that atoms can be excited to higher energy states by the absorption of electromagnetic energy (usually ultraviolet or visible light). The energy bands in which each element absorbs are very narrow and are specific for that element. Treatment of the theoretical aspects of this subject is beyond the scope of this report; the reader is referred to the classical work of Herzberg [3-2] for further information.

#### 3.3.2 Practical Considerations [3-3, 3-4]

In order to accomplish analysis by atomic absorption, the element sought must first be reduced to the elemental state i.e., freed from all chemical bonds to other elements, vaporized and interposed in a radiation beam from the excitation source. In most instances, this is accomplished by drawing a solution of the sample, as a fine mist ("nebulized"), into a suitable flame. Recently, however, a technique has been introduced which accomplished specimen atomization within a heated graphite tube [3-5, 4-18]. This has removed a number of the problems which are related to the stability of "atomization" process (see e.g., the basic paper of Kahn [3-6]); in addition, due to its ability to produce somewhat higher temperatures which are uniform over a greater optical path length, the "furnace" method (used in this work) offers greater sensitivity. This is especially important in the determination of the more refractory elements, such as aluminum and titanium.

The electromagnetic radiation is generally produced by a hollow-cathode lamp. The cathode of this device contains the element of interest and thus emits a line spectrum which corresponds specifically to that

element. The sample absorbs electromagnetic energy at the resonance lines as it is excited to a higher energy state. The amount of energy absorbed is proportional to the concentration of the element in the sample and is quantitatively measured by comparison of the energy density of the chosen resonance line before and after absorption by the sample.

### 3.3.3 Equipment

The necessary equipment to perform atomic absorption analysis is generally contained in one instrument (such as the Perkin-Elmer Model 303 used in this work, Figure 3-4) which has the following major components:

- (1) light source, generally a hollow cathode lamp
- (2) chopper
- (3) monochromator
- (4) photodetector
- (5) sample atomizer

The sample atomizer can be either the common flame nebulizer using premixed gases or the more recently developed graphite tube furnace attachment [4-18] employed in the current studies. In addition to the higher absolute analytical sensitivity of the AAS method when the latter introduction system is used, the graphite tube sampler has the advantages of minimal sample requirement (with sample sizes typically in the range from 5 to 50  $\mu$ l) as well as the capability to concentrate the sample prior to the vaporization step.

The graphite tube is heated by passing approximately 400 amperes at 10 volts through its 2" length, yielding a fairly uniform temperature of about 2800 to 2900°K within the tube, effectively vaporizing the sample.

### 3.3.4 Experimental Procedure

The use of the atomic absorption spectrometer with a graphite tube sampler is relatively simple. An analysis consists of the injection of the sample or standard into the graphite tube with a microsyringe, vaporizing it, passing it through a monochromatic light beam and recording the measured absorption of the chosen radiation line on a strip chart recorder. Calculation of the quantity of element can be made by reference to a standard calibration curve or by the method of additions.



FIGURE 3-4: PERKIN-ELMER ATOMIC ABSORPTION SPECTROMETER WITH GRAPHITE FURNACE



### 3.3.5 Sensitivity and Detection Limits

As pointed out by Kohn [3-6], a distinction should be made between sensitivity and detection limits. The former is defined as the concentration of an element in water solution which will produce an absorption of 1% (.0044 absorbance units). Sensitivities for the elements of interest in the current work are presented in Table 3-1. Detection limits are a function of both sensitivity and instrumentation characteristics such as stability and signal-to-noise ratio. A generally accepted definition for the detection limit is the concentration in water solution which gives a signal twice the size of the variability of the background. Since this is a function of the peculiarities of each instrument, etc., no meaningful generalization can be made other than that the detection limit in a well designed system can be considerably lower than the reported sensitivities.

TABLE 3-1  
SENSITIVITIES IN THE GRAPHITE TUBE FURNACE AAS [3-7]

<u>ELEMENT</u>	<u>SENSITIVITY</u> <u>Picograms/1% Absorption</u>
aluminum	120
chromium	25
copper	50
iron	30
manganese	8
nickel	140
titanium	2,000
vanadium	350

### 3.3.6 Discussion of Errors

A variety of sources of error exists in AAS, many of which are related to sample introduction and the "atomization" process which precedes

the absorption. These include analytical interferences, the atomization vaporization and dispersion processes, instrumentation (both optics and electronics) and procedural. Each will be discussed briefly, in turn.

Analytical "interferences" generally fall into three categories: (1) chemical (usually incomplete dissociation of compounds analyzed; (2) ionization (shifting the absorption wavelength), and (3) matrix (desensitization or enhancement due to the nature of the sample solution). Use of the graphite furnace usually removes the "chemical" interferences, but may aggravate that due to ionization. For the systems studied, only aluminum has an ionization potential low enough (5.96 ev) to be of any concern. This was obviated by serendipity; in those samples where corrosion of the 6Al-4V titanium was most favored (the chloride-doped) the more readily ionized sodium (5.12 ev) was presented to "shield" the aluminum. Matrix effects were sought, but not detected in this set of experiments.

The difficulty in obtaining reproducibility in the atomization, vaporization and dispersion processes are considered to be responsible for the largest analytical uncertainties [3-4]. Contributing to this are such things as fluctuation of the furnace temperature, absorption of the solvent (hydrazine) on the wall of the furnace, variations in the flow of inert gas through the furnace and sample condensation ("fuming") at the tube openings. At the 30-50% absorption level, it is stated that coefficient of variation of precision is of the order of 5% for aqueous solvents and 15% for organic solvents [4-18]. Just where hydrazine would fall on this scale is not known.

Instrumentation errors arise from such things as: dispersion and scattering in the optics, yielding "fuzzy" lines and losses in intensity; instabilities in the hollow cathode tube, resulting in fluctuations in the intensity of the excitation source; photomultiplier stability; and electronic "noise". The latter determines the detection limit of the apparatus, since this factor is typically defined as the concentration (in water solution) which gives a signal twice the size of the variability of the background [3-6]. Thus at the detection limit the element can be determined with a coefficient of variation of 50%.

Procedural errors can arise from such things as rate of sample introduction; poor selections of, or variations in, the solvent evaporation /char/ elemental vaporization sequences; and improper selection of sample size (optimum size yields an absorption 10 to 100 times the sensitivity value, i.e., ppm per 1% absorption. This optimum is often not achieved when concentrations are in the parts per billion range.

It has been stated [3-4] that "under usual conditions the relative error (accuracy) associated with AAS is of the order of 1 to 2 percent". This undoubtedly assumes replicate sampling of well-behaved aqueous solutions of the element sought, with little or no interference and a stable instrument. As indicated earlier, however, precision is of the order of  $\pm 15\%$  for non-aqueous solvents, and can vary by as much as 50% at the detection limit, for any given element. The samples analyzed by AAS in the course of this program were typically one of a kind, i.e., there were few replicated conditions, and little or no opportunity to reduce scatter by means of statistical manipulation. Consideration of these facts, together with the variety of ways in which error may be introduced led to the conclusion that any AAS value produced in this program should probably be enclosed in an error band of  $\pm 25\%$ . This estimate received some validation in studies of the 304L CRES/hydrazine system, where the average scatter about the mean values of metals found in the blanks was  $\pm 23\%$ .

#### 4.0 EXPERIMENTAL VERIFICATION OF THE PREDICTION METHOD

Essential to the development of a viable method for predicting long-term compatibility between propellants and materials is the orderly laboratory verification of that method. As laboratory tests are completed, the prediction method can be modified or added to as required to produce the best possible tool. An integral part of the prediction method is the characterization of the interactions that take place between the propellant and material. For the most part, it is only through laboratory testing that these interactions can be identified and quantified.

The experimental work was accomplished by the investigation of the following four significant systems:

- (1) 6Al-4V titanium with liquid fluorine ( $LF_2$ )
- (2) 2219-T87 aluminum with  $LF_2$
- (3) 304L CRES with hydrazine
- (4) 6Al-4V titanium with hydrazine

In addition to the above systems, the following systems were investigated but at a lower level of effort:

- (5) 6Al-4V titanium with FLOX (88:12)
- (6) 304L CRES with monomethylhydrazine (MMH)
- (7) 6Al-4V titanium with MMH

#### 4.1 THE 6Al-4V TITANIUM / LIQUID FLUORINE SYSTEM

##### 4.1.1 System Definition and Application

The 6Al-4V titanium alloy is a widely used aerospace material possessing excellent physical and chemical properties. The alloy is nominally 90% titanium with 6% aluminum and 4% vanadium. Typical alloys also contain approximately 0.1% iron. The 6Al-4V Ti ELI (extra low interstitial grade) is characterized by its excellent properties at low temperatures.

Fluorine is one of the most powerful oxidizing chemicals known, reacting with practically all organic and inorganic substances. Its energy as a rocket oxidizer is unsurpassed by any known oxidizer. Under static conditions, fluorine reacts slowly with many metals at room temperature and often forms a metal fluoride film on the surface of the metal which retards further reaction. At liquid fluorine temperatures, reaction with metals is even slower. Commercial fluorine is about 99% pure with up to 0.3% hydrogen fluoride and carbon tetrafluoride by weight. The remainder of impurities are generally oxygen, nitrogen, and other inert substances.

The application of this particular system is somewhat undefined for this work, but several assumptions can be made. The overall application would be an unmanned spacecraft whose mission would include some of the outer planets. This would imply several conditions which include: zero gravity, low temperature and pressure environment, and the possibility of micrometeoroid impact. Because of its high strength to weight ratio, titanium would be favored for large structures such as the propellant tank. For a propellant such as  $\text{LF}_2$ , the temperature would be between 78° and 85°K.

#### 4.1.2 Preliminary Exposure Test

There is a significant amount of history available for the 6Al-4V titanium  $\text{LF}_2$  system. Salvinski, et al [4-1], Uney and Fester [4-2], and Vander Wall, et al [4-3] have published excellent reviews of compatibility data for this system. There are conflicting data on the shock sensitivity of titanium in liquid fluorine; however, it is well established that in static systems 6Al-4V titanium is suitable for use with  $\text{LF}_2$ . Furthermore, no instances of propagation of reaction in  $\text{LF}_2$  have been reported for impact studies [4-4]. Corrosion rates for most metals in  $\text{LF}_2$  are very slow (after the initial film formation), but data on the rates of reaction are scarce.

Since the available data for the 6Al-4V titanium  $\text{LF}_2$  system indicated that there would be no problem in a static system, the preliminary exposure test was bypassed.

#### 4.1.3 Determining the Rate of Metal Buildup in $LF_2$

##### 4.1.3.1 Selecting the Measurement Technique

One of the most promising techniques for predicting long term interaction between propellant and material is the use of the rate of metal buildup in the propellant as an indicator of that interaction. Referring to Figure 2-4, we can see that the measurement technique must first be selected. The procedure for making that selection is shown. 6Al-4V titanium has no major element which has a long-lived radioisotope; iron is not considered to be present in sufficient quality to be useful, therefore, the radioactive tracer technique is not applicable. Since the propellant  $LF_2$  is a cryogenic material, the dry activation analysis technique is chosen.

##### 4.1.3.2 Selecting the Test Apparatus and Configuration

Certain restrictions are placed upon the design of the test apparatus as a result of the chosen measurement technique and the propellant. First of all, for the container, there are a number of possible materials that can be considered. These are shown in Table 4-1. The proper choice would have a "NO" answer in each column for the case that we are considering. There is only one material that meets all the qualifications for this test, viz FEP Teflon. This material has the added features that it is relatively transparent (compared to TFE Teflon for example) and it is thermoplastic.

The configuration for this measurement technique is not critical, but the size should be kept small for two reasons: One, the volume of  $LF_2$  should be kept to a minimum for safety; and two, the overall diameter may be restricted by the reactor ancillary equipment.

##### 4.1.3.3 The Detailed Immersion Test

Insofar as possible, the detailed immersion test will be discussed by reference to Figure 2-3.

TABLE 4-1  
POSSIBLE CONTAINER MATERIALS FOR T1 - LF<sub>2</sub> TEST

	ACTIVATES IN REACTOR ?	CONTAINS METAL IMPURITIES ?	REACTS WITH PROPELLANT ?	REACTS WITH IMPURITIES ?
GLASS	YES	YES	NO	YES
QUARTZ	NO	NO	NO	YES
METAL	YES	YES	YES	YES
POLYETHYLENE	NO	NO	YES	NO
FEP TEFLON	NO	NO	NO	NO

Specimen Coupons - The 6Al-4V titanium was obtained in the form of 1-mil foil from Teledyne Rodney Metals in Pico Rivera, California. The titanium was the standard annealed type with heat number G4628. Composition was determined to be 5.88% aluminum, 3.82% vanadium, and 0.15% iron. The balance was titanium. The foil was cut into coupons 2.5 cm by 3.2 cm. No special surface finish treatment was given. Each coupon was numbered with a steel stamp.

The coupons were cleaned according to the following procedure: wash in absolute ethanol, soak in 50% concentrated  $\text{HNO}_3$ /50% water solution for ten minutes at room temperature, rinse with distilled - deioniz water to a neutral pH, and dry.

The coupons were then weighed on a Mettler balance (certified accuracy  $\pm .25$  mg), and bagged in polyethylene until ready for use.

Two coupons were used for each test container to increase the available surface area.

Test Fluid - The fluorine used in this test conformed to specification MIL-P-27405 and was supplied by the Allied Chemical Corporation, General Chemical Division, Morristown, New Jersey. Prior to test, the fluorine was passed through a sodium fluoride column to remove hydrogen fluoride. After such treatment, the gas contained less than 0.015% HF by volume as determined by infrared spectrometry according to the MIL specification. Hydrogen fluoride was added to the fluorine in various amounts for certain tests.

Some difficulty was encountered during the investigation of HF impurity that is worth reporting. The mil spec for  $\text{F}_2$  calls for an infrared analysis of HF in fluorine and specifies use of a stainless steel gas cell with calcium fluoride windows. Since a nickel-plated steel cell with barium fluoride windows was available and had been used previously for this type of analysis, this was used first. A general fogging of the  $\text{BaF}_2$  windows was noted although such was not deemed detrimental to the analysis of HF. Difficulty arose, however, when lower concentrations of HF in argon were being analyzed while preparing a calibration curve. The material



that fogged the windows apparently released HF when exposed to very low concentrations of HF in the diluent argon, giving erroneous results. Subsequently, a mil spec stainless steel cell with  $\text{CaF}_2$  windows was fabricated and a new calibration was attempted. Essentially the same performance was noted with the new cell: the windows fogged and HF was liberated at low HF concentrations in argon. Consequently, the  $\text{CaF}_2$  windows were replaced with fluorinated ethylene propylene windows which worked quite well, being impervious to both HF and  $\text{F}_2$ . With this cell no anomalies were noted and the concentration of HF in  $\text{F}_2$  was found to be 0.015% by volume.

Test Geometry - A convenient geometry for tests of this type is a cylindrical tube approximately 2.5 cm in diameter and various lengths up to 40 cm. The coupon surface area to liquid volume ratio (S/V) was approximately  $0.5 \text{ cm}^{-1}$ . The coupons were held in the tube by friction along the tube walls. Two coupons were used in each tube. See Figure 4-1.

Container Design - The test container was constructed from FEP Teflon and stainless steel. The portion of the container that contacted the liquid fluorine was all FEP Teflon and that part which connected to the gas handling system was stainless steel. The Teflon portion was constructed from 2.54 cm (1.0 inch) FEP tubing and .127 cm (.05 inch) FEP sheet obtained from the Fluorocarbon Company, Anaheim, California. A bottom for the tubing was prepared from a 2.86 cm diameter disk cut from the sheet stock and joined to the tubing using the heat from a small hot plate. See Figure 4-2. The completed tube was slipped over the 2.54 cm stainless steel tubing, the end of which was polished to provide a vacuum-tight sealing surface. The Teflon tube was then heated slightly in a burner flame to soften the Teflon and then allowed to cool on the steel tube, shrinking in the process and forming a tight seal. The container was connected to the gas handling system via a Nupro stainless steel bellows valve. See Figure 4-3.

Instrumentation - No internal instrumentation was used for this test. All measurements were performed by post-test analyses. It was possible to monitor, as necessary, the internal pressure of the test container by means of the pressure gage used for the gas handling system. This gage was a

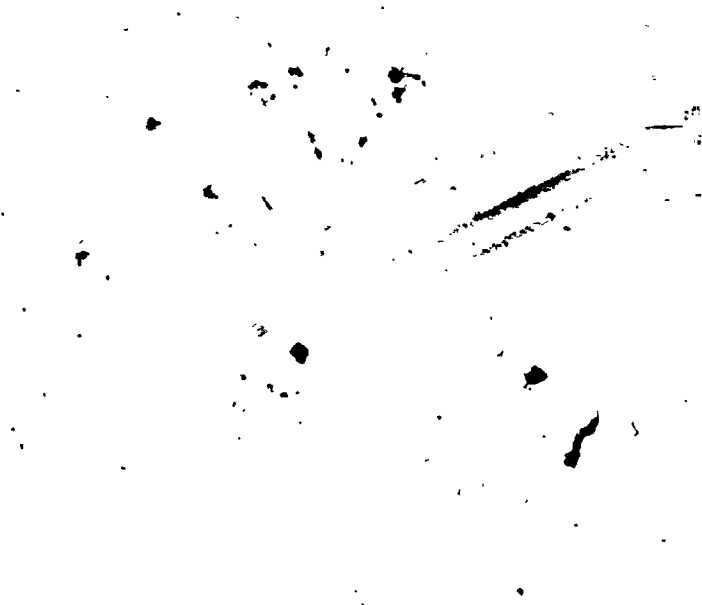


FIGURE 4-1: TEST CONFIGURATION FOR 6A1-4V TITANIUM/FLUORINE, FLOX SYSTEMS

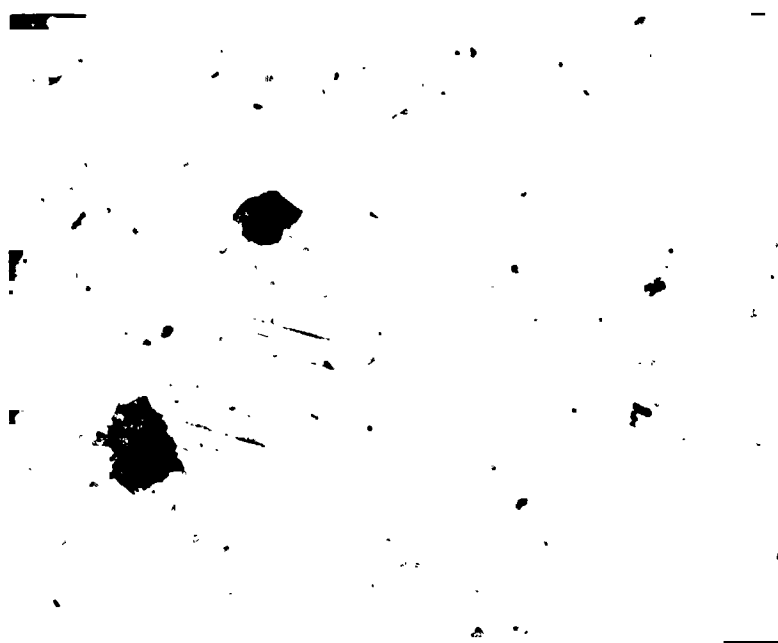


FIGURE 4-2: PREPARATION OF THE FEP TEFLON CONTAINER

monel Bourdon gage designed specifically for use with fluorine systems. Temperature of the liquid fluorine was controlled by a liquid nitrogen or liquid oxygen bath as required.




FIGURE 4-3: STORAGE CONTAINER FOR 6 A1-4V TITANIUM/FLUORINE SYSTEM

Test Conditions - Conditions for this test were those shown in Table 4-2. The basic temperature chosen was that of liquid nitrogen. Often  $\text{LF}_2$  is stored at a pressure slightly above atmospheric; this pressure can be obtained by using liquid oxygen for the temperature bath. The hydrogen fluoride content of the  $\text{LF}_2$  was varied from .008 to 0.4 percent by weight.

Test Setup - A schematic diagram of the fluorine handling system is shown in Figure 4-4. The fluorine system is a standard design recommended by Allied Chemical Corporation. Two test containers can be connected to the system at once, or alternately a test container can be disconnected from the system during test to allow other equipment to be attached. Figure 4-5 shows two storage containers connected.

TABLE 4-2  
TEST CONDITIONS - Ti LF<sub>2</sub>

TEST NO.	TEMPERATURE °K	PRESSURE Atm.	HF CONC. Wt. %	DURATION Hours
1	77.7 ↓	.41 ↓	0.008 ↓	1.0
3				4.8
5				10.0
6			0.1 ↓	40.0
4				100.0
13				4.0
14			0.2 ↓	40.0
15				100.0
10				4.0
11			0.4 ↓	40.0
12				100.0
7				4.0
8	90.2 ↓	1.63 ↓	0.008 ↓	40.0
9				100.0
22				4.0
23			↓	40.0
24				100.0

Test Procedure - The clean test container with coupons is attached to the fluorine handling system and evacuated. Gaseous fluorine is admitted to the system to perform the passivation process and the pressure slowly increased to one atmosphere and held for 10-15 minutes [4-5]. The system is again evacuated and then the fluorine condensation into the test container is started. If hydrogen fluoride is to be added to the container, a tube with a weighed amount of HF is attached to the system and fluorine gas is used to flush the HF into the LN<sub>2</sub> cooled storage container. The F<sub>2</sub> pressure is successively raised to one atmosphere and then allowed to condense into the test container until the pressure drops to about 1/2 atmosphere. This is repeated ten times; this procedure transfers 99.9% of the HF into the test container by successive dilution. When the HF transfer is completed, the F<sub>2</sub> pressure is raised to slightly above atmospheric pressure and the condensation process is continued until the required amount of liquid fluorine is obtained. The valve on the container is then closed and the container can be disconnected from the handling system if required.

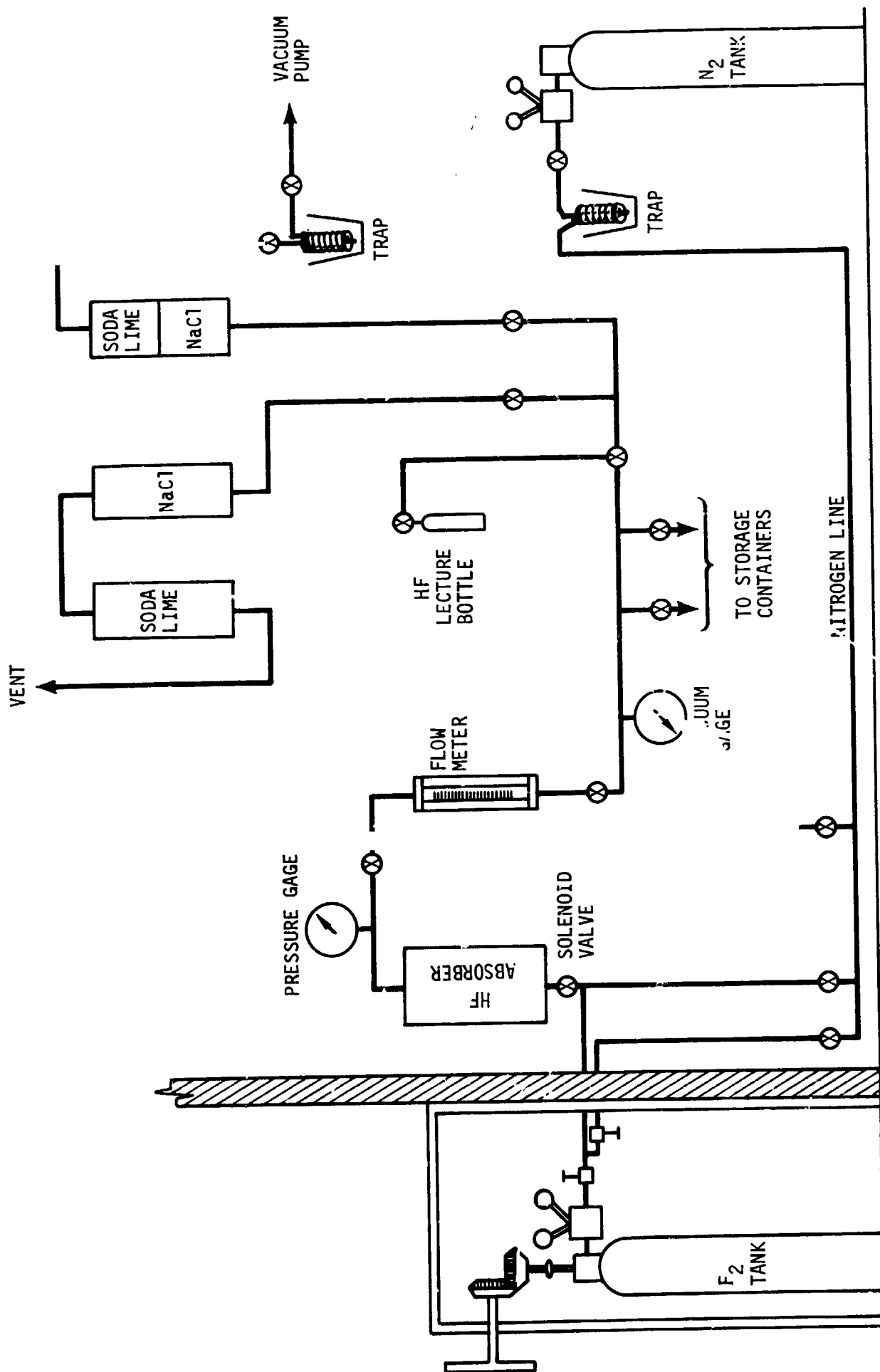


FIGURE 4-4: FLUORINE OXIDIZER HANDLING SYSTEM.

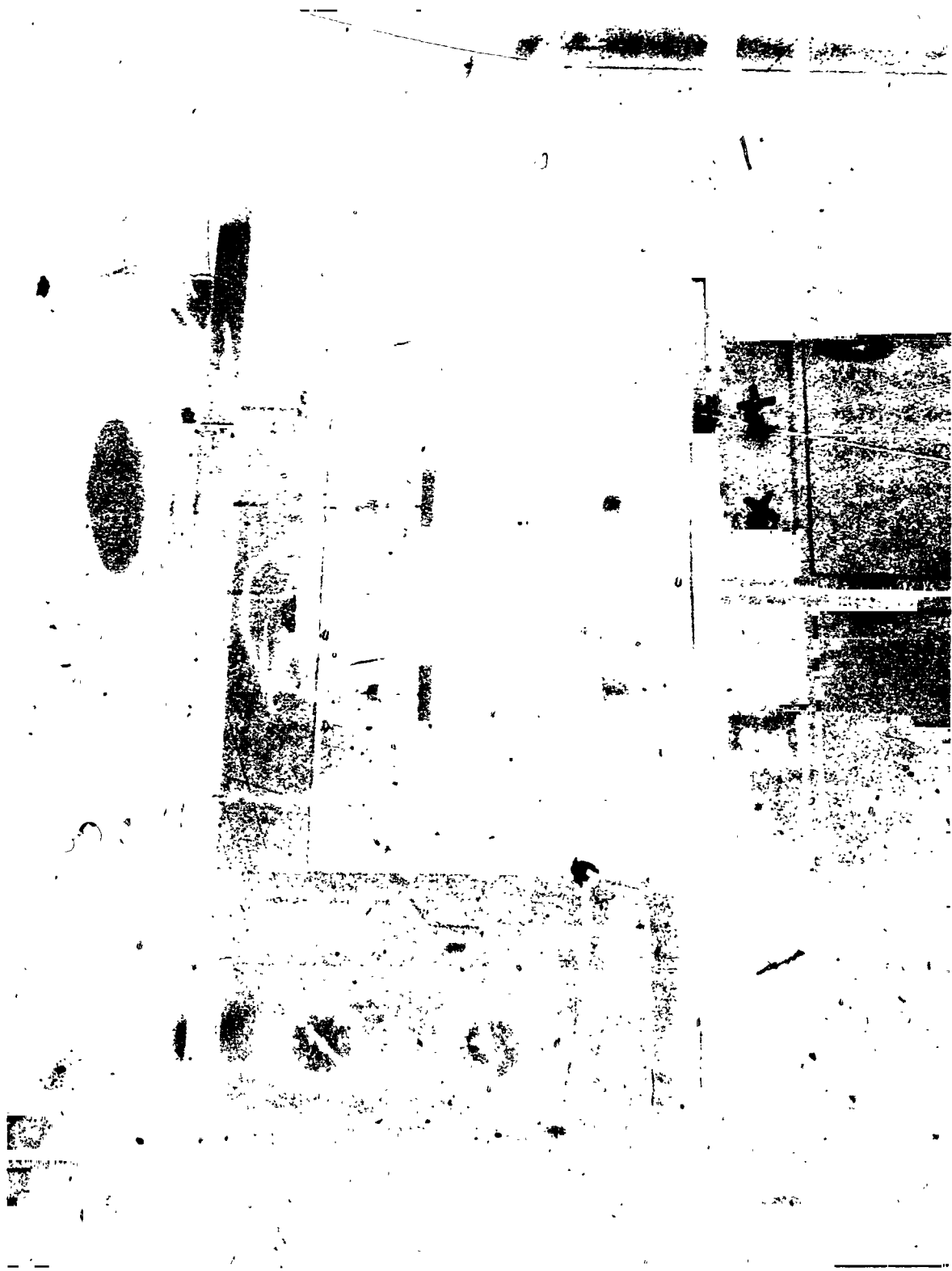
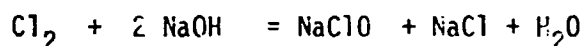
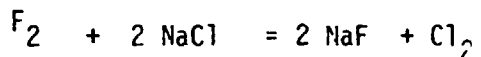


FIGURE 4-5: VIEW OF 6AL-4V TITANIUM-FLUORINE TEST SETUP

Test Termination - At the completion of the test time, the  $\text{LF}_2$  in the test container is allowed to warm slightly, raising the pressure to somewhat above atmospheric and the gaseous fluorine is vented through the NaCl and soda lime reactors to the atmosphere. The reaction in the reactors are as follows:



The boil-off takes about 20-30 minutes for a 25 gram sample. After the  $\text{LF}_2$  has been evaporated, the system is quickly flushed with nitrogen to minimize the contact time of the coupon with any residual gases. The bottom of the tube (about 3.3 cm) is then cut off and the metal coupons are weighed and sealed in a polyethylene bag. The bottom of the tube which contains any residue left after the evaporation is also sealed in a clear polyethylene bag.

Post-Test Measurements - The distillation of the  $\text{LF}_2$  from the test container leaves behind a residue which presumably contains traces of the metals constituting the coupon. The analysis for titanium, aluminum, and vanadium was performed by neutron activation analysis. An analysis of the fluorine gas after the test was not performed because the evaporating gas was not representative of the mixture in the container; the added HF, if any, remained in the container until all of the fluorine had evaporated. The volume required to contain all of the 25 grams of fluorine as a gas at room temperature and produce a homogeneous mixture would be about 16 liters; this volume was not available in the gas handling system. The amount of HF in the system was determined by weighing the "HF container" before and after delivery of the HF to the storage container. Corrections were made for fluoride film formation in the container and for weight of fluorine gas left in the container.

The neutron activation analysis of the residue in the FEP tubes was subcontracted to the Lawrence Livermore Laboratory (LLL) in Livermore, California, primarily because of the high detection sensitivity at that facility. As a preliminary investigation and baseline measurement, the metal contents of the FEP Teflon were determined. The results of that analysis showed 7.2 micrograms ( $\mu\text{g}$ ) Ti, 3.6  $\mu\text{g}$  Al; and .018  $\mu\text{g}$  V for a typical nine-gram Teflon test container. This high metal content was completely unexpected since Teflon was reported to have contaminants in the parts per billion range [4-6].

Since it was anticipated that the level of metals in the residue would be of the order of a few hundred nanograms or as much as a microgram, the activation of the metals in the Teflon would obscure any such metals in the residue. Therefore, it was decided that the residue must be removed from the FEP Teflon tube.

A procedure for removing the residue from the Teflon tubes was successfully developed by the Lawrence Livermore Laboratory. This procedure is detailed in Appendix B. The residue was transferred to a small Durathane bag and freeze dried.

A thorough examination of the contribution of reagents and blank vessels to the metal analysis was performed by LLL. Several blank runs were made: a reagent blank, with 2 ml 3N HCl in a Durathene bag; a sample blank, with 2 ml 3 N HCl rinsed in a blank Teflon tube; and a spiked sample, with 1 ml of solution containing 2 micrograms each of Al, V, and Ti dried in a blank Teflon tube subsequently transferred to a Durathane bag. No titanium or vanadium was contributed from empty Teflon tubes, but an erratic amount of aluminum was found. The metals found in reagents used were negligible; the contribution from blank Durathane bags was not. The values for the overall blanks were 140.3 nanograms (ng) Ti, 599 ng Al, and 4.07 ng V. The high value for aluminum caused difficulty in the analysis for aluminum in the residue samples, about half of the samples had an amount of aluminum that was less than or equal to the blank (background).

Other post-test measurements included the washing of the metal coupons in distilled water, drying at 345°K, and weighing.

#### 4.1.4 Correlation of Metal Buildup to Propellant - Material Reaction

Looking at the compilation of the test results in Table 4-3 and Figure 4-6, several meaningful observations can be made. First of all, with few exceptions, those tests in which hydrogen fluoride was added to the fluorine exhibit higher titanium content in the fluorine residue than those without it. This is true also to a lesser extent for vanadium, more so at the higher HF concentrations. The data for aluminum are of little value for two reasons:



TABLE 4-3  
TEST RESULTS-6A1-4V TITANIUM IN LIQUID FLUORINE

Temp. °K	HF Wt. %	Duration Hr.	Ti ppb	V ppb	V/Ti Ratio	Al ppb	Foil Numbers	Initial Mass, mg	Final Mass, mg	Δm, mg	Mass after Washing, mg	Δm from Initial mass, mg	Remarks
77.7	.008	1	†	Ø	-	207 ± 10.5	1, 2	171.26	172.47	+1.21	173.00	+1.74	Clean
		4.8		.92 ± .08	-	16.7 ± 9.1	5, 6	171.82	173.04	1.22	173.66	1.84	Some film
		10	7.8 ± 3.5	.78 ± .07	.10	Ø	9, 10	171.88	172.36	.48	172.92	1.04	Discolored, shiny
		40	7.5 ± 3.9	2.67 ± .10	.36	82.0 ± 9.1	11, 12	172.26	172.75	.49	173.31	1.05	Bright, shiny
		100	5.0 ± 4.8	.87 ± .08	.17	19.2 ± 9.1	51, 52	172.89	174.09	1.20	173.78	.89	Some film, tarnish
	.1	4	5.4 ± 2.6	.39 ± .07	.071	†	27, 28	173.3	175.9	2.6	173.64	.34	Film remains, bright otherwise
		40	8.4 ± 2.3	.54 ± .07	.064	†	21, 22	173.1	175.2	2.1	173.99	.89	Much film
		100	12.1 ± 3.5	.84 ± .08	.069	12.0 ± 9.1	37, 38	170.62	171.57	.95	172.25	1.63	Film, tarnish
	.21	4	3.9 ± 2.1	.21 ± .07	.053	Ø	35, 36	171.21	172.30	1.09	172.72	1.51	Film, tarnish
		40	260 ± 12	9.64 ± .24	.037	10 ± 9.1	25, 26	172.0	176.77	4.77	172.85	.85	Very corroded, esp #26
		100	12.3 ± 3.6	.45 ± .07	.037	26 ± 9.1	29, 30	172.35	178.89	6.54	170.13	-2.22	Still bright, shiny, little film
	.38	4	165 ± 29	6.67 ± .24	.040	14.2 ± 9.1	15, 16	179.5	183.1	3.60	180.59	+1.09	Film, tarnish
		40	53.5 ± 5	4.79 ± .14	.090	†	19, 20	172.1	175.4	3.3	172.59	.59	Film, tarnish
		100	200 ± 13	2.88 ± .13	.014	57 ± 9.1	17, 18	172.6	175.9	3.3	171.48	-1.12	Film remains, bright otherwise
90.2	.008	4	7.4 ± 2.5	.17 ± .07	.023	9.1 ± 9.1	31, 32	175.71	176.17	.46	176.12	+.41	Some film, spotted
		40	4.2 ± 2.6	.89 ± .08	.212	23.1 ± 9.1	33, 34	171.01	172.52	1.51	172.83	1.81	Some film, some tarnish
		100	5.0 ± 2.5	.33 ± .07	.066	†	23, 24	176.23	176.45	.22	177.11	.88	Tarnished, purplish

KEY  
 Ø Sample - Blank ≤ 0.0  
 † Sample - Blank ≤ Analytical error  
 + None Detected

Detection Limits:  
 Ti = 2.1 ppb  
 V = .07 ppb  
 Al = 9.1 ppb

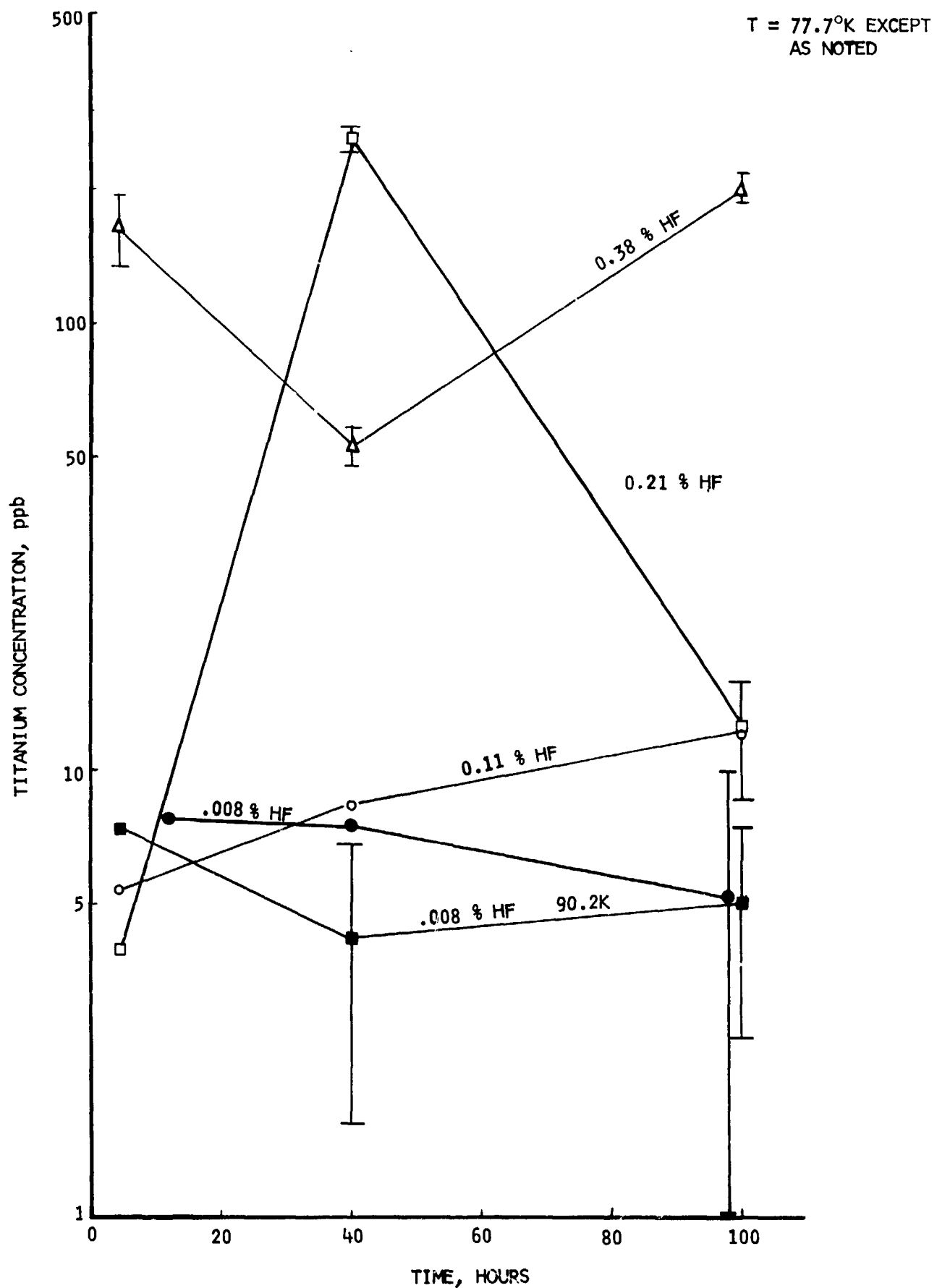


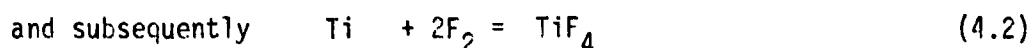
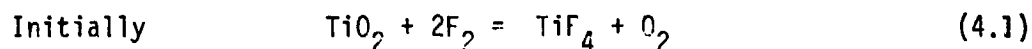
FIGURE 4-6: TITANIUM CONCENTRATIONS IN LIQUID FLUORINE,  
DEPENDENCE ON HF AND TIME

(1) Large analytical errors were encountered during analysis because of the high aluminum found in the blank determination; and (2) suspected contamination of samples with aluminum ("aluminum gets into everything").

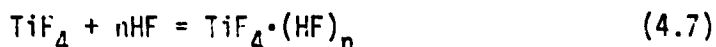
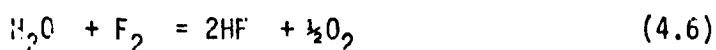
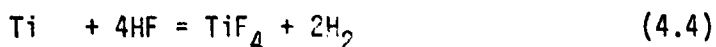
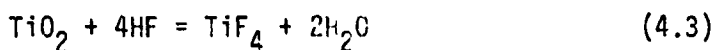
Secondly, the values for metals found in the residue do not appear to correlate directly to duration of the test. This result is anomalous to basic kinetics and is discussed in further detail below.

Noting the changes in mass of the coupon specimens, we see that, after washing with hot water, many of the specimens increased in mass. This increase signifies that the fluoride film was simply hydrated rather than dissolved. Schmidt [4-7] reports that "fluoride films ... are so closely bonded to the metal surface that they are considered "in" rather than "on" the surface of the metal." Thus a thin, closely bonded fluoride film might not be expected to be soluble. On the other hand, as the film thickens from continued reaction or from influence of HF, the outer portion is not bonded so tightly to the base metal and dissolution of at least part of the film becomes possible. This is indeed noted in Table 4-3. Those specimens which exhibited large mass increases before washing, lost significant amounts of mass upon washing. Visual examination of the washed samples revealed, however, that even they retained some fluoride film after washing so that the overall change in mass does not represent the mass of the fluoride film formed.

Quantifying the above observations into some meaningful order must involve an understanding of the reactions taking place. There are several possible reactions which contribute to the corrosion process. Consider the following:



Competing with these reactions are



An attempt to determine the overall reaction mechanism and rate from these equations is a task for a computer. For now, we must be satisfied to make some general comments about the observed results.

The major reaction product  $\text{TiF}_4$  is not significantly soluble in liquid fluorine and one would not expect the hydrofluoride adduct  $\text{TiF}_4 \cdot (\text{HF})_n$  to be soluble either. However, it is well established [4-1] that in the case of many metals, hydrogen fluoride destroys the metal fluoride film and causes increased corrosion. The exact mechanism is not understood, but probably the HF alters the crystal structure of the film sufficiently to expose additional base metal which is oxidized by the  $\text{F}_2$ . The reaction is likely similar to that of moisture hydrating fluoride films [4-9]. This cyclic mechanism may continue until the HF is used up or the base metal is depleted.

One can postulate that random amounts of  $\text{TiF}_4$  or  $\text{TiF}_4 \cdot (\text{HF})_n$  are flaked off the surface and are either suspended in the  $\text{LF}_2$  or settle to the bottom of the vessel.

The analysis of the  $\text{LF}_2$  residue by neutron activation analysis suggests that some random factor is in play and that the level of metals found is difficult to directly relate to the amount of base metal reacted. Visual examination also revealed that film formation was more pronounced in certain areas.

Those samples exposed only to relatively pure  $\text{LF}_2$  (0.008% HF) showed very little Ti present in the residue and the coupon surfaces exhibited the least amount of interaction. The tarnish observed on some samples was indicative of a very thin fluoride film and could not be washed off. Kleinberg and Tompkins [4-10] found that the film on titanium in fluorine at 192°K reached a constant thickness of about 6 Å after four hours.

Thus, while there is an evident lack of correlation of the results with time, there is a definite correlation with the amount of hydrogen fluoride present. While some authors [4-2] have indicated that no attack should occur below the freezing point of HF (181°K), the present work does not bear out that assumption. The method used to introduce HF into the fluorine was conducive to the formation of very finely divided particles of

HF, and one cannot assume that all chemical reactivity stops simply because of a change of state. The solubility of HF in liquid fluorine is not well known, but even minute amounts of dissolved HF can be considered to account for the observed results. One estimate of HF solubility in  $LF_2$  places the limit at 0.3% by weight [4-12].

Examination of the values of V/Ti ratio in Table 4-3 reveals that for the cases in which HF was added to the fluorine, the value for the ratio is very close to the value in the alloy (.042). On the other hand, those tests for which no HF was added (.008% HF) showed significantly higher values of the V/Ti ratio. The average value for tests with HF added was .046, and that with no HF added was .155. These numbers are suggestive of a difference in the mechanism that is responsible for the appearance of titanium and vanadium in the liquid fluorine.

Any attempt to explain this difference in behavior would be pure speculation; however, it is plain that the hydrogen fluoride plays an important, albeit undefined, role in the contamination of the fluorine with titanium and vanadium. This role may involve the formation of the  $TiF_4 \cdot HF_n$  adduct (see Equation 4.7) in the surface film which may crack or otherwise deform the crystal structure of the film permitting further attack on the base metal. If this cracking and other micromechanical movement causes some of the film to be lost to the solution, a concentration of metals in the solution may be much closer to the nominal value found in the alloy than otherwise would be the case.

#### 4.1.5 Establishing the Kinetic Rate Expression

Although the data generated here do not permit a definite kinetic expression to be established, it is still possible to utilize kinetic rate law arguments to formulate long-term predictions. This is possible because the data may be sufficient to set an upper limit or maximum rate of corrosion in the system of interest.

As previously noted in Section 2.3, the most injurious reaction is an autocatalytic attack on the metal surface. An example of such a mechanism is the decomposition of hydrazine in the presence of a copper

compound. The decomposition is catalyzed by copper ions, and as the reaction progresses, more and more copper ions are added to the solution, thereby accelerating the rate of corrosion. While such highly destructive mechanisms are possible in other propellant systems, they are unknown in metal-fluorine systems. Furthermore, hydrazine is logically susceptible to autocatalytic decomposition, since the compound is thermodynamically unstable. In the 6Al-4V titanium/fluorine system, however, no such comparable situation exists.

Having ruled out autocatalytic mechanisms, the next worst case is a zero-order reaction. In such an instance the rate of reaction is independent of contaminants in the propellant and is constant as a function of time. Zero-order reactions are relatively common in metal/liquid systems. Pseudo-zero-order reactions are especially common. See Section 2.3. While the reaction may technically depend on the surface area of the metal or the concentration of the propellant, these variables remain essentially constant during the course of the reaction, which in turn leads to a constant corrosion rate.

It will now be assumed that the data of Table 4-3 reflect a zero-order rate law as the worst possible case. Although there is some scatter in the data, the data points can be averaged to obtain a reasonable upper limit to the rate expression. Table 4-4 summarizes the results for titanium.

Inspection of Table 4-4 shows that at low HF concentrations (0.008 and 0.11%) the rate of titanium buildup in fluorine is greatest at short contact times. Such a result is not consistent with a zero-order reaction, but rather is suggestive of a higher-order reaction rate. At higher HF concentrations (0.21 and 0.38%) the data becomes more erratic, but in all four cases the trend is toward a higher corrosion rate at higher HF concentrations as indicated by averaging the three data points at each HF concentration. These average corrosion rates can be assumed to be of zero-order in order to calculate the maximum possible rate. These rates are plotted against HF concentration in Figure 4-7. The solid line represents a least-squares fit to the experimental data. Figure 4-8 illustrates the maximum extent of titanium buildup as a function of time.

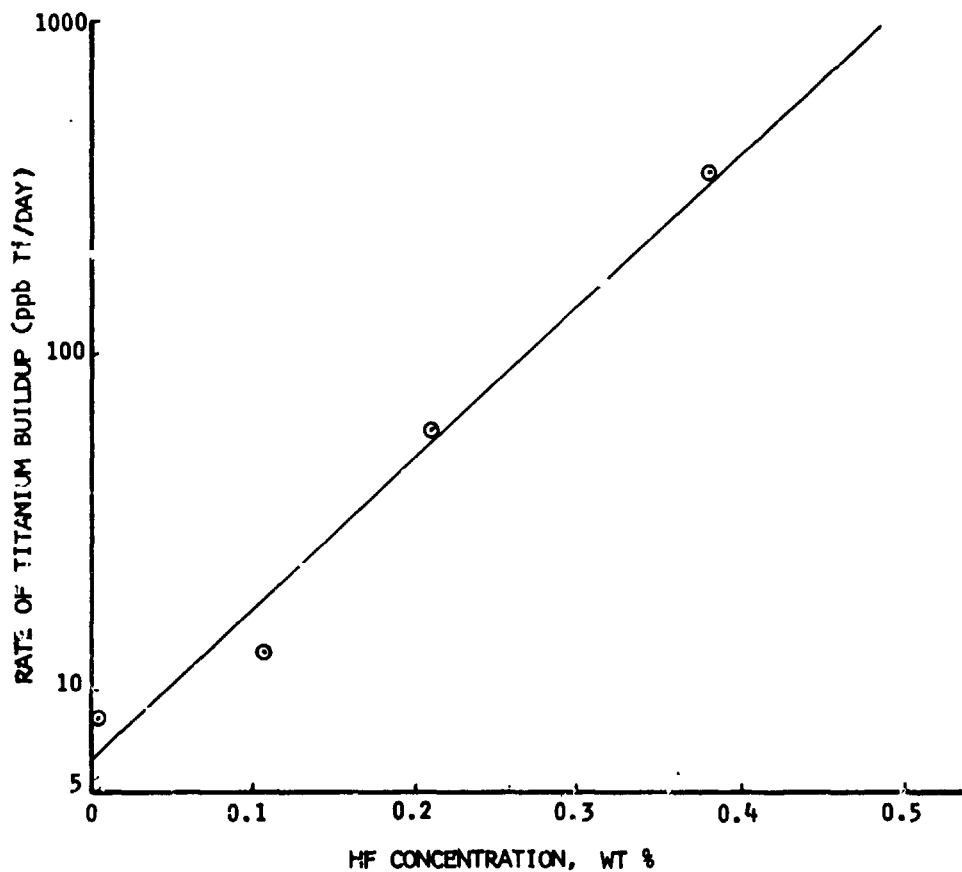


FIGURE 4-7: RATE OF TITANIUM BUILDUP IN LIQUID FLUORINE AS A FUNCTION OF HF CONCENTRATION ASSUMING ZERO - ORDER KINETICS

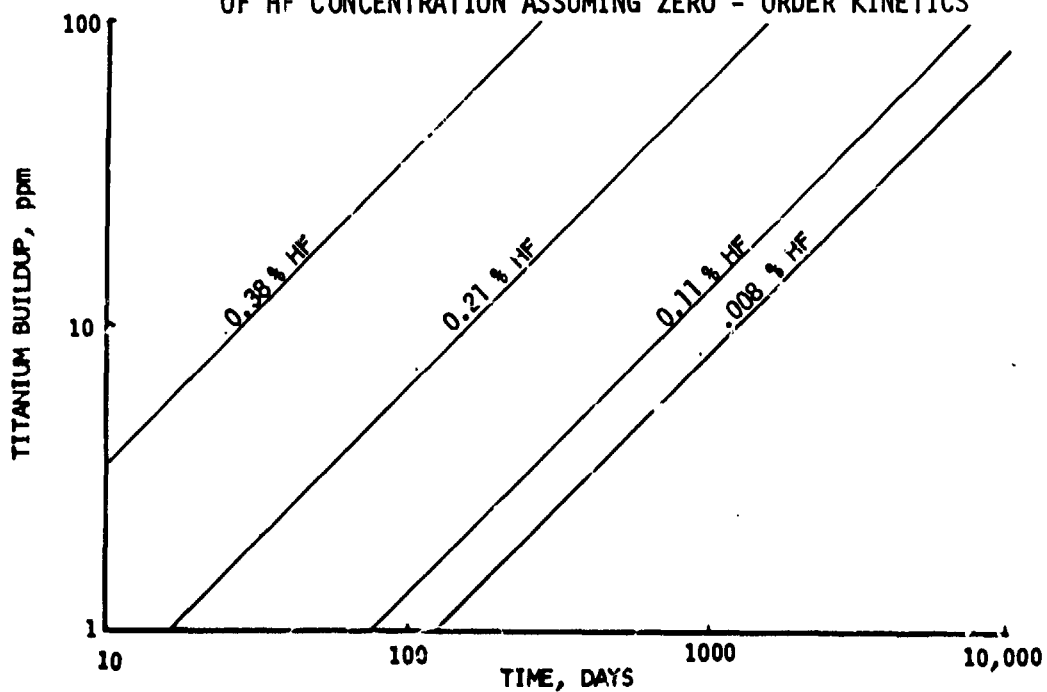


FIGURE 4-8: TITANIUM BUILDUP IN LIQUID FLUORINE AT 77.7°K AS A FUNCTION OF TIME ASSUMING ZERO - ORDER KINETICS

TABLE 4-4

AVERAGE RATE OF TITANIUM BUILDUP IN FLUORINE AT  
77.7°K

HF (Wt.%)	DURATION (Days)	Ti (ppb)	Ti (ppb/day)	Ti ppb/day (average of 3 rates)
0.008	0.17	7.8	18.6	8.1
	1.67	7.5	4.5	
	4.16	5.0	1.2	
0.11	0.17	5.4	31.8	13.2
	1.67	8.4	5.0	
	4.16	12.1	2.9	
0.22	0.17	3.9	22.9	60.5
	1.67	26.0	155.7	
	4.16	12.3	3.0	
0.38	0.17	165	970.6	350.2
	1.67	53.5	32.0	
	4.16	200	48.0	

#### 4.1.6 Integration of Results

Integration of the results from the pressure leg (see Figure 2-1), the metal leg, and the surface leg was as follows: the pressure buildup, if any, was below the detectable limit for this test. The metal buildup has been discussed. The surface degradation, while observed, was not quantified



by means other than mass change and examination by optical microscope at 30X. As noted in Table 4-3, those samples in the presence of large amounts of HF exhibited what was termed in Figure 2-5 as "gross changes". No detailed study of the surface change of those samples would be warranted. Since no "gross" changes were noted for those samples immersed in HF-free  $\text{LF}_2$ , detailed surface studies of those samples may yield significant data. The scope of this program did not permit such a study, however.

#### 4.1.7 Predicted Long Term Behavior

As an illustration of a hypothetical use of the prediction method, assume that liquid fluorine (maintained at 77.7°K) is loaded into a 6Al-4V titanium feed tank (surface-to-volume ratio  $0.5 \text{ cm}^{-1}$ ) of a spacecraft. Analysis of the fluorine shows an HF impurity content of 0.04%. How long can the spacecraft remain in space before the titanium builds up to a level of 10 ppm?

The problem is solved by finding the maximum possible average rate of corrosion corresponding to 0.04% HF in Figure 4-7. According to the graph,

Max. possible Ti buildup rate = 9.0 ppb/day. A lower limit to the time required to reach 10 ppm is then given by

$$\begin{aligned} \text{Time (years)} &= \frac{(10 \text{ ppm}) (10^3 \frac{\text{ppb}}{\text{ppm}})}{9.0 \text{ ppb/day}} \left( \frac{1 \text{ year}}{365 \text{ days}} \right) \\ &= 3.0 \text{ years} \end{aligned}$$

#### 4.2 THE 6Al-4V TITANIUM/FLOX (88:12) SYSTEM

Because of its close relationship to the previous system, the 6Al-4V titanium/FLOX (88:12) system will be discussed now.

#### 4.2.1 System Definition and Application

FLOX (88:12) is a mixture of nominally 88% fluorine by weight and 12% oxygen. In many respects, the properties of FLOX are similar to those of  $LF_2$ . It has been shown that the reactivity of FLOX is less than that of fluorine, depending upon the percentage of fluorine in the mixture [4-7]. FLOX (88:12) is not a standard commercial gas and must be made up specially for each requirement. FLOX is made by mixing gaseous fluorine with gaseous oxygen and then condensing to the liquid state as required.

The application for this system is essentially the same as that for fluorine with the FLOX and fluorine being alternate choices.

#### 4.2.2 Preliminary Exposure Test

There is very little literature on the subject of compatibility of FLOX (88:12) with titanium, but most authors indicate that caution should be exercised with this system. The sensitivity of titanium in liquid oxygen to shock with propagation [4-8] and the shock sensitivity under some circumstances in liquid fluorine suggest that shock sensitivity in FLOX would be a serious consideration. Thus, any tests with this system should be approached with due respect.

The reactivity of FLOX can be assessed in two ways. Firstly, the FLOX can be considered as liquid fluorine which has been diluted with liquid oxygen, and therefore the reactivity is proportionately less [4-7]. Secondly, the FLOX can be considered to have essentially the reactivity of fluorine (at high percentages of fluorine) plus having the contribution due to liquid oxygen with its potential for forming reactive free radicals. Thus, a case can be made for either decreased reactivity or increased reactivity of FLOX compared to  $LF_2$ .

Because of favorable experience with the titanium/fluorine system and the high content of fluorine in the FLOX, the preliminary exposure test was bypassed but the detailed immersion test was approached with caution.

#### 4.2.3 Determining the Rate of Metal Buildup in FLOX

Because of the close similarity between FLOX (88:12) and  $\text{LF}_2$ , the procedures and techniques used for determining the metal buildup in FLOX were the same as used for  $\text{LF}_2$ , described in Section 4.1.3. The 6Al-4V titanium/FLOX system was investigated at a lower level of effort than the fluorine system, thus the test conditions were abbreviated. See Table 4-5.

The FLOX was prepared by adding gaseous oxygen to a cylinder of gaseous fluorine. Analysis of the mixture yielded a value of 87.1% fluorine by weight; however, for reasons of consistency, the FLOX will be referred to as 88:12.

#### 4.2.4 Correlation of Metal Buildup to Propellant - Material Interaction

The results of the metal buildup study of 6Al-4V titanium in FLOX (88:12) are shown in Table 4-6 and Figure 4-9. Many of the comments for the 6Al-4V titanium/ $\text{LF}_2$  study apply to this system also. The same scatter in the data was noted, and there was the same difficulty in correlating the metals found in the FLOX with the surface reaction. The observation that HF plays an important role in the interaction was reinforced and the nature of the fluoride films was about the same. The films were noted to be very tenacious and could not be completely removed. It was noted also that the loss in weight of the coupon upon washing was related to the film thickness. That is, the very thin films were not soluble in water, whereas the thicker films found after exposure to FLOX with HF added, wash off, at least in part.

It is interesting to note again the ratio of vanadium to titanium found in the residue. For the tests in which HF was added, the ratio is very near that found in the alloy, whereas with no HF added the vanadium is high by up to an order of magnitude. This again suggests that the HF may attack both metals equally while the  $\text{F}_2$  may preferentially attack the vanadium. Alternately, the titanium fluoride film may be substantially more adherent than the vanadium fluoride layer in the presence of fluorine only but less adherent in the presence of HF.

TABLE 4-5

## TEST CONDITIONS FOR THE 6A1-4V TITANIUM/FLOX SYSTEM

Test No.	Temperature °K	Pressure Atm.	HF Conc. Wt %	Duration Hours
16	77.7	.37	0.008	4
17	↓	↓	0.008	40
18			0.008	100
19			0.4	4
20			0.4	40
21	77.7	.37	0.4	100

TABLE 4-6

TEST RESULTS, 6A1-4V TITANIUM IN FLOX AT 77.7°K

HF Wt. %	SOAK TIME Hr.	Ti ppb	V ppb	A1 ppb	Foil Numbers	Initial Mass, mg	Final Mass, mg	$\Delta m$ mg	Mass After Wash, mg	$\Delta m$ From Initial mg	Remarks
.008 ↓	4	3.3 ± 3.2	.49 ± .08	73.8 ± 9.2	43,44	170.60	170.56	-.04	171.20	+.60	Tarnish, some spots
	40	14.1 ± 5.5	4.6 ± .1	†	41,42	172.37	173.03	+.66	173.37	1.00	Tarnish, very little film
	100	* +	8.8 ± .5	†	39,40	175.14	177.54	2.40	175.19	.05	Some film, spots
0.43 ↓	4	408 ± 18	20.6 ± .5	†	47,48	171.44	174.38	2.94	170.29	-1.15	Some film
	40	110 ± 7	4.6 ± .1	†	45,46	173.58	179.16	5.58	172.56	-1.02	Film remaining
	100	158 ± 10	7.4 ± .2	†	49,50	159.46	172.44	2.98	168.70	-.76	Film remaining

\* Deposits noted inside tube after evaporation.

Also noted dark-orange-red ring in FEP tube at the top of LN<sub>2</sub> level which melted to a dark-red liquid on warming.

## KEY

Ø Sample - Blank &lt; 0.0

† Sample - Blank &lt; Analytical Error

+ None Detected

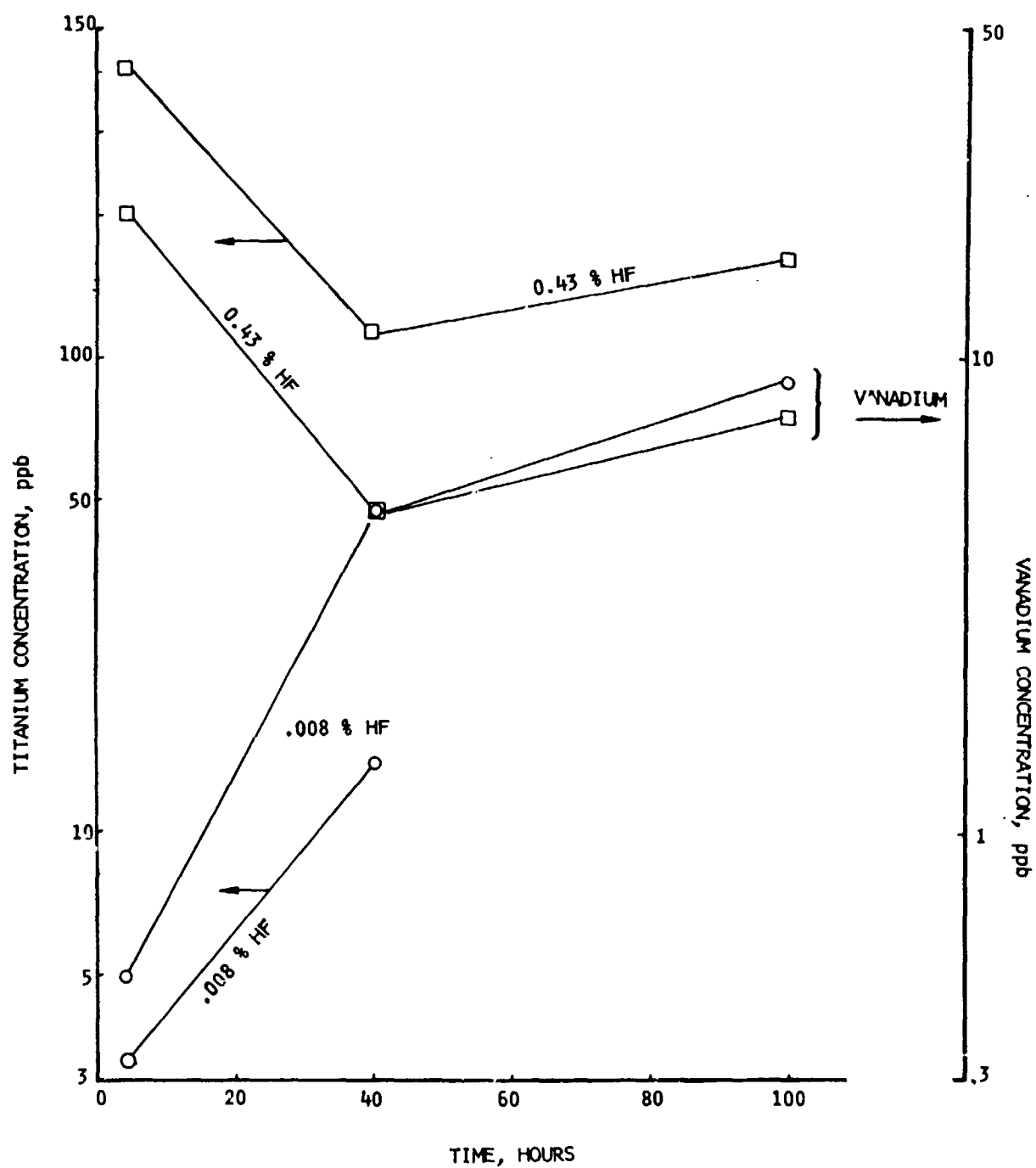


FIGURE 4-9: TITANIUM AND VANADIUM CONCENTRATIONS IN FLOX, DEPENDENCE ON HF AND TIME

Little significance can be given to the one case in which aluminum was detected in sufficient quantity to report. The same difficulties with quantifying aluminum in the fluorine tests were also associated with the FLOX tests.

#### 4.2.5 Establishing the Kinetic Rate Expression

The data of the FLOX test are similar to the data of the fluorine test in that the scatter in the data do not permit the derivation of a definite kinetic expression. However, arguments similar to those of Section 4.1.5 can again be used to establish a maximum possible rate of metal buildup assuming zero-order kinetics.

Focusing on the element titanium, the data of Table 4-6 can be used to construct Table 4-7. Insufficient data are available from the abridged FLOX test to obtain a meaningful dependence of the rate of metal buildup on HF concentration. Nevertheless, the data of Table 4-7 are suggestive of a higher corrosion rate at higher HF concentrations (Cf. Tai 4-4).

#### 4.2.6 Integration of Results

Integration of the results from the pressure leg, the megal leg and the surface leg was as follows: any possible pressure buildup (doubtful) was below the limit of detection. The metal buildup has been discussed. The surface degradation was noted through visual examination at 30X and through measurement of the mass changes as noted in Table 4-6. Significant mass changes were observed in cases with 0.4% HF in the FLOX and as in the case for  $LF_2$  no detailed study would be warranted for such a level interaction. Furthermore, since the major emphasis of the program was on the metal buildup, no detailed surface study was pursued for the HF-free FLOX case.

#### 4.2.7 Predicted Long Term Behavior

A hypothetical situation can be used to demonstrate the prediction method. Suppose that it is desired to send a spacecraft on a five year mission. The titanium feed tank ( $C/V = 0.5 \text{ cm}^{-1}$ ) is to be loaded with FLOX at 77.7°K. Can the HF content of the FLOX be reduced to a sufficiently low level upon passing the FLOX through a column packed with NaF to limit the amount of titanium buildup to no more than 20 ppm at the end of the mission?

TABLE 4-7

## AVERAGE RATE OF TITANIUM BUILDUP IN FLOX AT 77.7°K

HF (Wt.% )	Duration (days)	Ti (ppb)	Ti (ppb/day)	Ti ppb/day (Average of 3 rates)
0.008 ↓	0.17	3.3	19.4	9.3
	1.67	14.1	8.4	
	4.16	0	0	
0.43 ↓	0.17	408	2400	334.6
	1.67	110	65.9	
	4.16	158	38.0	

An attempt can be made to answer the question posed above by assuming, as indicated in Section 4.2.5 (also Cf. 4.1.5) that the rate of titanium buildup can occur no faster than that defined by zero-order kinetics. Table 4-7 shows rate data for FLOX that has been passed through NaF, thereby reducing the HF concentration to 0.008%. The average rate of titanium buildup was found to be 9.3 ppb/day. An upper limit to the titanium expected after 5 years is then given by

$$\text{Titanium (maximum)} = \frac{9.3 \text{ ppb}}{\text{day}} \times \frac{1 \text{ ppm}}{10^3 \text{ ppb}} \times \frac{365 \text{ days}}{\text{year}} \times 5 \text{ years} = 17 \text{ ppm}$$

Therefore, the answer to the question posed in the preceding paragraph is, yes, the amount of buildup will be below the specified limit.



TABLE 4-8

CHEMICAL COMPOSITION OF 2219-T87 ALUMINUM  
(% By Wt.)

ELEMENT	SPECIFICATION	TEST SAMPLES
Copper	5.8 - 6.8	6.03
Manganese	0.2 - 0.4	.26
Iron	0.3 max.	.23
Silicon	0.2 max.	.11
Zinc	0.1 max.	.088
Vanadium	0.05 - 0.15	.09
Titanium	0.02 - 0.10	.08
Magnesium	.02 max.	.014
Zirconium	.10 - .25	.16
Aluminum	Balance	Balance

#### 4.3 THE 2219-T87 ALUMINUM/LIQUID FLUORINE SYSTEM

##### 4.3.1 System Definition and Application

The 2219-T87 aluminum alloy is another promising aerospace material possessing excellent physical and chemical properties. The alloy belongs to a family of aluminum alloys which have a high percentage of copper; 2219-T87 possessing 5.8 to 6.8 percent. The general specification for 2219-T87 aluminum is shown in Table 4-8.

The oxidizer fluorine and the application have been described in Section 4.1.1.

##### 4.3.2 Preliminary Exposure Test

Aluminum in general is regarded as being acceptable for fluorine service [4-2] and stress corrosion of 2219-T87 aluminum in  $LF_2$  has been investigated by Loentz [4-11] who found negative results. Because of the favorable data available for 2219 aluminum, no preliminary exposure test was necessary.

#### 4.3.3 Determining the Rate of Metal Buildup in $LF_2$

##### 4.3.3.1 Selecting the Measurement Technique

In Figure 2-4, the method for selecting the proper measurement technique was shown. Since 2219 aluminum contains copper as one of the major alloy constituents and since copper-63 activates to the 12.8-hour half life copper-64 radioisotope, the radiotracer technique is a good choice for the measurement technique. Refer to Section 3.2 for background and theory for this technique.

##### 4.3.3.2 Selecting the Test Apparatus and Configuration

The constraints on the container material are not as great as for the dry activation analysis technique, but the FEP Teflon tubing was found to be quite satisfactory for fluorine service and was convenient to use. The FEP Teflon tube was attached to a copper tube in the same manner as discussed in Section 4.1.3.2. The copper tube was bent into an angle to provide a method for proper shielding of the gamma detector from the radioactive sample. See Figure 4-10.

##### 4.3.3.3 The Detailed Immersion Test

Specimen Coupons - The 2219-T87 aluminum was obtained from the Aluminum Company of America (Alcoa) in the form of 2.18 mm (0.125 inch) sheet, Alcoa heat number 720471. Samples of the sheet were milled to 0.125 mm and coupons were cut to size (25 mm x 13 mm). The thickness of the coupons was kept to a minimum to keep the total radioactivity of the samples to a minimum. The chemical composition of 2219-T87 aluminum is given in Table 4-2.

The coupons were cleaned and passivated according to the procedure which included the following steps:

- (1) Degrease with isopropyl alcohol.
- (2) Wash in 4% Joy solution for 5 minutes at 350° to 370°K.
- (3) Deoxidize in 4% solution of  $Na_3PO_4$  at 350°K for 2 minutes.
- (4) Rinse with distilled water.
- (5) Passivate with a solution of 1% HF, 1%  $HNO_3$ , and  $H_2O$  for one minute at room temperature.
- (6) Rinse with distilled water to a neutral pH.
- (7) Dry with dry, oil-free nitrogen.

A view of one of the cleaned and passivated coupons is shown in Figure 4-11. Two coupons were used for each test to double the available surface area.

Test Fluid - The fluorine used was identical to that described in Section 4.1.3.3 for the 6Al-4V titanium/fluorine investigation.

Test Geometry - The test geometry consisted of the two 2219 aluminum coupons suspended in the angle tube by a ribbon of pure aluminum foil (1100-0) which was, in turn, connected to a Teflon covered magnetic stirring bar. See Figure 4-10. This configuration allowed external manipulation of the test coupons with the aid of a magnet after the container was sealed. The coupon S/V was approximately  $0.8 \text{ cm}^{-1}$ .

Container Design - The design of the test container was essentially the same as the one for the 6Al-4V titanium test with the exception that a long copper tube bent to an angle of  $30^\circ$  to  $45^\circ$  was used. This long tube allowed the radioactive 2219 aluminum coupon to be retracted to an area shielded from the detector by lead bricks as shown in Figure 4-12 or Figure 4-13.

Instrumentation - The internal pressure of the test container was monitored by the gas handling system pressure gage. The temperature of the container was controlled by a liquid nitrogen or liquid oxygen bath as required. The buildup of the copper-64 radioisotope in the fluorine was monitored by a NaI(Th) detector, dual-channel analyzer system consisting of the following apparatus:

- (1) 3" x 3" cylindrical sodium iodide crystal detector.
- (2) Boeing built preamplifier.
- (3) Baird-Atomic Dual Channel Analyzer, Model CS 202.
- (4) Baird-Atomic Timer, Model CS 905.
- (5) Baird-Atomic Scaler, Models CS 107 and CS 127.
- (6) John Fluke DC High Voltage Power.
- (7) Miscellaneous calibration sources.

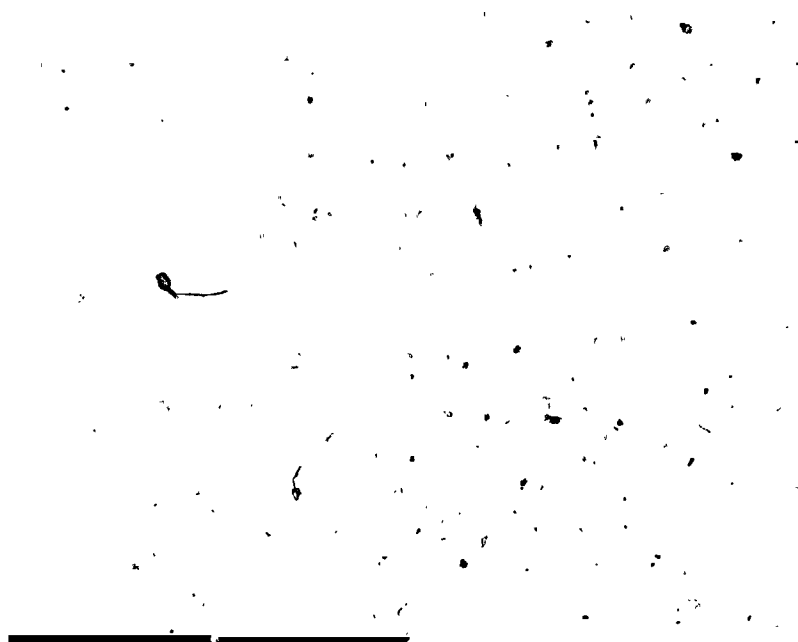


FIGURE 4-10: 2219 ALUMINUM TEST CONFIGURATION

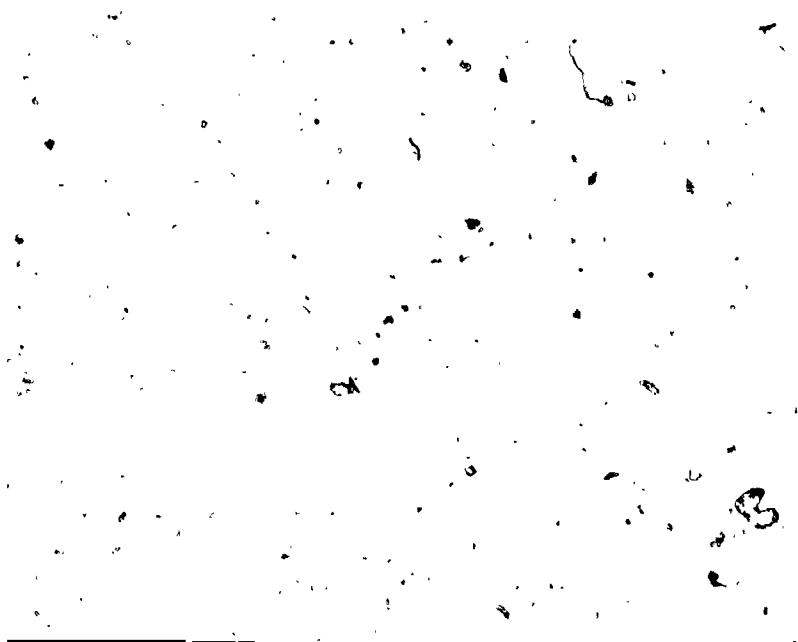


FIGURE 4-11: 2219 ALUMINUM SPECIMEN COUPON

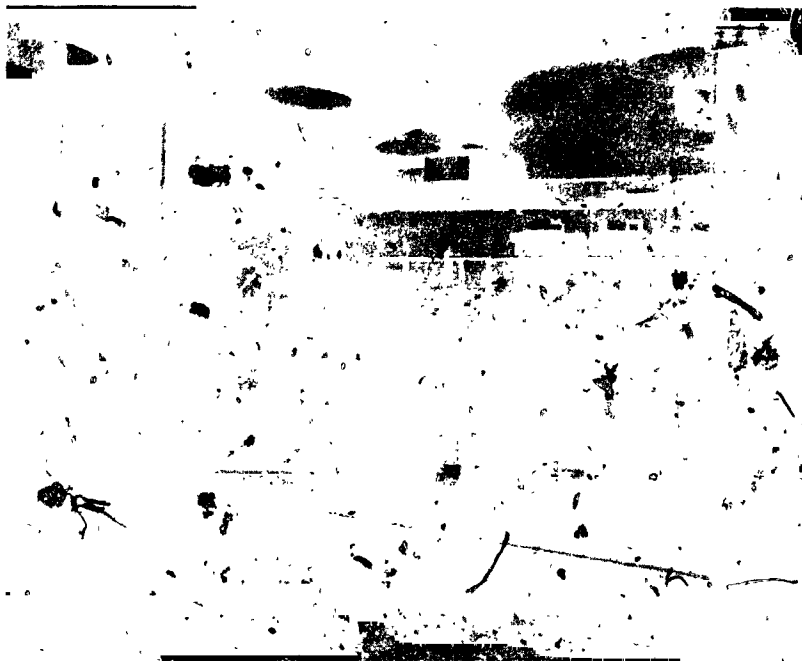


FIGURE 4-12: OVERALL TEST SETUP, 2219 ALUMINUM -  $\text{LF}_2$



FIGURE 4-13: CLOSE UP OF SETUP IN COUNTING CONFIGURATION

Test Conditions - The conditions used during the 2219 aluminum tests are shown in Table 4-9.

Test Setup - The fluorine handling system described in Section 4.1 3.3 was utilized for this test. Only one storage container was connected to the system during test. An overall view of the test setup is shown in Figure 4-12.

Test Procedure - The clean and dry storage container with the activated coupons in the retracted position was connected to the fluorine handling system and then evacuated. Gaseous fluorine was admitted to the system to passivate the storage container and coupons and the pressure was slowly increased to one atmosphere and held for 10-15 minutes. The system was then evacuated again to remove any possible HF and the condensation of the fluorine into the container was begun. If hydrogen fluoride was to be added to the container, a tube with a weighed amount of HF was attached to the system and fluorine gas was used to flush the HF into the storage container where it was condensed along with the fluorine by liquid nitrogen. When the HF transfer and fluorine condensation were complete, the fluorine source valve was closed and the container was left open to the handling system so that the pressure could be monitored.

With the proper amount of fluorine in the storage container, a count of background radiation was made and then the 2219 aluminum coupons were lowered into the fluorine to begin the test.

During the test, the coupons were periodically withdrawn from the  $LF_2$  into the area shielded from the detector and the amount of radioactive copper-64 in the  $LF_2$  was measured. Then the coupons were returned to the  $LF_2$  and the test continued.

Test Termination - After about five days, the disintegrations of copper-64 became too few to count in a reasonable length of time and the testing with the 2219 aluminum coupon was terminated. The coupons were

retracted from the  $LF_2$  which was then allowed to warm slightly, raising the pressure slightly above atmospheric. The gaseous fluorine was vented through NaCl and soda lime reactors to the atmosphere. The storage container was disconnected from the fluorine handling system and the specimen coupon was removed and weighed. The bottom of the Teflon tube was cut off at the level of the top of the liquid exposure and sealed in a polyethylene bag.

Post-Test Measurements - The residue left in the FEP Teflon tube after the fluorine evaporation was analyzed for aluminum and copper by atomic absorption spectroscopy (see Section 3.3). The residue was soluble in water.

The aluminum coupons were washed thoroughly in hot water, rinsed with distilled water, dried at 345°K, and weighed. The results are shown in Table 4-10.

#### 4.3.4 Correlation of Metal Buildup to Propellant - Material Reaction

The results of the measurement of the rate of metal buildup in the fluorine from 2219 aluminum are displayed in Figure 4-14. The uncertainties in the data points is approximately  $\pm 20\%$ . After about 100 hours, the copper-64 tracer has decayed sufficiently so that it is no longer measurable.

For HF concentrations from .008% to .49% by weight in the liquid fluorine, there appears to be little difference in the rate of interaction with the 2219 aluminum. The scatter in the data is sufficiently large to obscure minor dependence, if any.

Increasing the temperature 16 degrees results in a small but measurable rate increase.

In general, the 2219 aluminum alloy is quite resistant to liquid fluorine, even with .49% HF present. The  $AlF_3$  film protecting the aluminum appears to be very effective as shown by the small mass changes recorded in Table 4-10. There, also, little significant difference is noted when HF is added to the fluorine.

TABLE 4-9

TEST CONDITIONS 2219-T87 ALUMINUM - LIQUID FLUORINE SYSTEM

Test No.	Temperature °K	Pressure Atm.	HF Conc. Wt. %	Duration Hours
25	77.7	.41	.008	78
27	77.7	.41	.12	104
26	77.7	.41	.49	117
28	90.2	1.63	.008	101

TABLE 4-10

ALUMINUM SAMPLES BEFORE AND AFTER EXPOSURE TO LIQUID FLUORINE

Test Number	Coupon Number	Initial Mass mg	Mass After Test mg	$\Delta M$	Mass After Wash mg	$\Delta M$
25	5	98.29	98.54	+.25	98.48	+.17
	6	97.62	97.98	+.36	97.87	+.25
27	8	107.47	107.93	+.46	107.63	+.16
	9	94.76	95.18	+.42	94.86	+.10
28	13	108.83	109.19	+.36	108.92	+.09
	16	107.04	107.30	+.24	107.23	+.19
26	18	104.56	104.70	+.14	104.75	+.19
	19	103.61	103.83	+.22	103.80	+.19



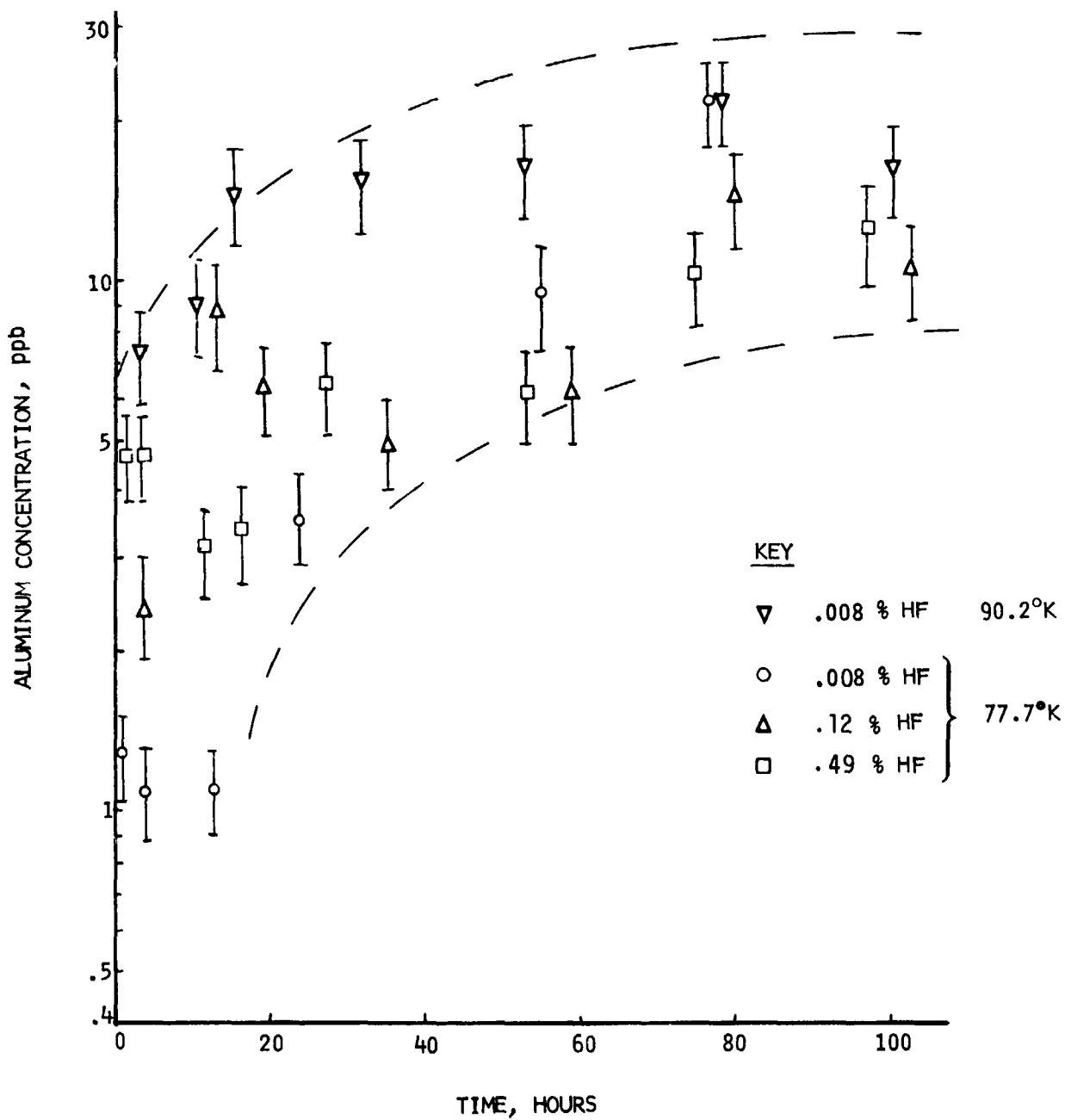


FIGURE 4-14: ALUMINUM BUILDUP IN LIQUID FLUORINE WITH TIME FROM CONTACT WITH 2219 ALUMINUM

#### 4.3.5 Establishing the Kinetic Rate Expression

For reactions in which the concentration of the product is very small compared to the reactants, most types of reactions (e.g., first-order, second-order, etc.) exhibit pseudo-zero-order rate dependence, that is, the rate of product accumulation is proportional only to time. With the small degree of interaction noted between the aluminum and fluorine, one would expect this type of dependence. Thus, a plot of aluminum concentration in fluorine versus time should yield a straight line. Such a plot is shown in Figure 4-15. The solid lines were constructed from a least squares treatment of the experimental data. Treatment of the 77.7°K data separate from the 90.2°K data indicates a definite dependence of the rate on temperature. The slope of the lines calculated by least squares is equal to the reaction rate constant at that temperature. A plot of  $\log k$  versus  $1/T$  will give the activation energy and the Arrhenius constant in the equation  $k = Ae^{-E/RT}$ . This technique is shown in Figure 4-16 with the resulting equation being  $k = .85 e^{-316/RT}$  (ppb/hr), where  $R$  is the gas constant in calories/deg. mol.

This kinetic rate expression is by no means a rigorously defined entity; however, it represents the best available at this time.

#### 4.3.6 Integration of Results

While a complete investigation of the pressure leg and surface leg (Figure 2-1) were not accomplished, no pressure buildup was observed and no discernible surface change was noted on the 2219 aluminum other than some slight discoloration on one sample. Since the sample coupons used in the metal buildup leg were radioactive, a post-test surface analysis was not performed.

#### 4.3.7 Predicted Long Term Behavior

Using the kinetic rate expression developed for 2219 aluminum in fluorine, a prediction can be made for the level of metal buildup in liquid fluorine in an aluminum tank over a period of, say, five years. Let us assume that the storage pressure is to be 1.1 atmospheres (16 psia) so that

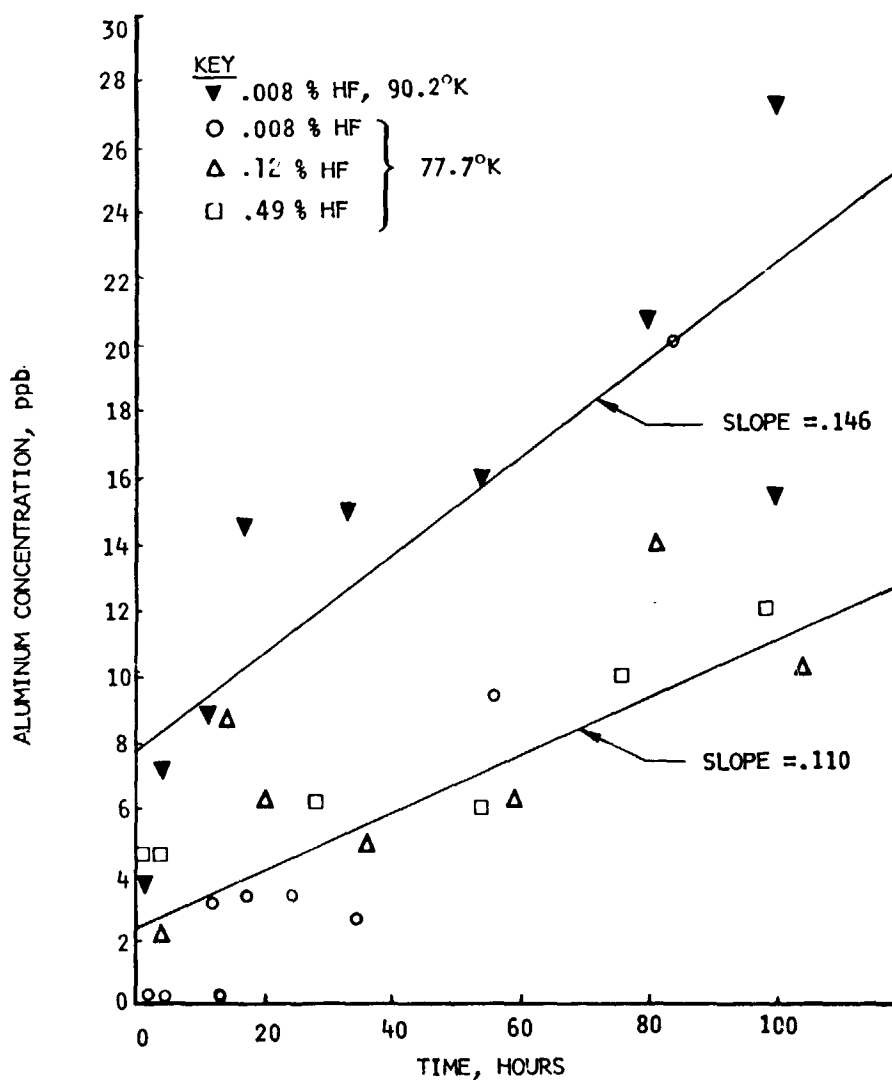


FIGURE 4-15: DERIVATION OF THE RATE CONSTANT FOR ALUMINUM BUILDUP IN LIQUID FLUORINE

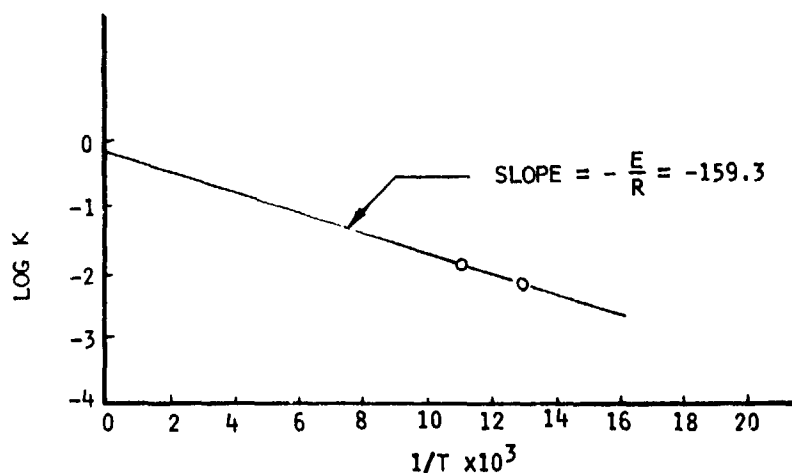


FIGURE 4-16: TEMPERATURE DEPENDENCE OF THE RATE CONSTANT

the temperature is 86°K. Also assuming an HF content within the range investigated in this work, we can calculate the reaction rate constant and determine the metal concentration after five years. The reaction rate constant is given by

$$k = .85 \exp [-216/(1.987 \times 86)] \text{ ppb Al/hr.}$$

$$k = .134 \text{ ppb Al/hr.}$$

The aluminum concentration at any time,  $t$ , is given by  $C_{Al} = k t$  where  $t$  is the time in hours. The mission duration in hours is 43,800 hours so that the aluminum concentration becomes 5.9 parts per million.

Now, let us consider another possible question; what average storage temperature can be endured during the five years and maintain the level of interaction low enough so that no more than 10 ppm aluminum is built up in the propellant? To produce a concentration of 10 ppm in five years would require a rate constant of .228 ppb/hr. Since  $\log k = \log .85 - (316) / (1.987T)$ , the temperature is 121°K. This is somewhat above a normal storage temperature ( $F_2$  vapor pressure ~14 atmospheres) and would not be expected to be encountered. Thus it is concluded that the interaction over the long term would be very low indeed.

#### 4.4 THE 6Al-4V TITANIUM/HYDRAZINE SYSTEM

##### 4.4.1 System Definition and Application

As the result of a detailed set of analyses considering trade-offs among the parameters of cost, mass and reliability, JPL has selected [4-13] a blowdown-pressurized monopropellant hydrazine propulsion system to provide trajectory correction impulse for outer planet flyby spacecraft. A typical example of such an application is the TOPS (Thermoelectric Outer Planet Spacecraft) vehicle for the Grand Tour mission. The advantages which accrue from the use of this energetic and thermodynamically unstable material are sufficiently great that all aspects of its use have come under close scrutiny. This combination of high reactivity and widespread applicability make hydrazine a most appropriate selection as the fuel to be studied in the current program.

Most commercial hydrazine, including that utilized in these studies, is purchased under Military Specification MIL-P-26536C. The latter requires a minimum hydrazine content of 98 percent (by weight), a maximum of 1.5 percent water (by weight) and a maximum particulate matter content of 10 milligrams per liter. This is a skeletal amount of information for a material which is subject to catalytic decomposition and has a requirement for storage and use in a spacecraft for periods up to ten years. This lack has been recognized and a revised Mil Spec is under preparation [4-14]. A recent investigation [4-15] reported that the major soluble non-metallic impurities are water, carbon dioxide, aniline and chloride ion; the major metallic ions are sodium, chromium, iron and nickel.

As mentioned previously (Section 4.1.1), the alloy designated as 6Al-4V titanium is widely used in aerospace applications because of its high strength-to-weight ratio, good machining characteristics and generally excellent chemical compatibility. Sufficient compatibility data has been gathered on this material to result in its provisional selection as the primary TOPS propulsion system material [4-13]. As discussed in

the latter reference and elsewhere, 6Al-4V titanium is one of the materials currently undergoing long-term hydrazine compatibility tests at JPL. The opportunity to develop parallel complementary data on the material of choice for hydrazine application made the decision to include 6Al-4V titanium both obvious and straightforward.

#### 4.4.2 Preliminary Exposure Test

All of the studies made to date on the 6Al-4V titanium/neat hydrazine system indicate a high degree of compatibility. The test data are extensive, and have been recently reviewed by Coulbert and Yankura [4-16] and by Cadwallader and Piper [4-17]. These results constitute a considerable portion of the justification for selection of this titanium alloy as the material of choice in TOPS propulsion systems. Since no new information would be obtained by conducting a preliminary exposure test on this system, this step was deleted.

#### 4.4.3 Determination of the Rate of Metal Buildup in the 6Al-4V Titanium/Hydrazine System

##### 4.4.3.1 Selection of the Measurement Technique

Selected sensitive techniques for determining the rate of metal buildup have been described in Section 3 and categorized as to their applicability in Section 2. Reference to Figure 2-4 shows that in the 6Al-4V titanium/hydrazine system (no long-lived radioisotope of major elements in the alloy, non-cryogenic propellant) modified atomic absorption spectroscopy yields the best results. In this context, "modified" specifically refers to use of the graphite tube furnace sampling method, in contrast to the more typical nebulizer flame technique [4-18]. Use of the former method enhances the sensitivity (i.e., allows detection of significantly smaller quantities) of refractory metals such as aluminum and titanium.

##### 4.4.3.2 Selection of the Test Apparatus and Configuration

There were essentially no constraints placed on the test apparatus and configuration which were related to the subsequent measurement technique. The modified atomic absorption method requires a very small sample size, typically 100 microliters or less. So long as the sample is submitted in a

container from which it is convenient to withdraw aliquots of this size with a microsyringe, the analyst is satisfied. The vessel delivered to the analytical laboratory need not be that in which the exposure was conducted. As a result, the only constraints were imposed by the desire to conduct the test simply, safely, and with a minimum opportunity for interference from the test capsule itself. All the requirements were met by the utilization of screw-cap type biological culture tubes, as detailed below.

#### 4.4.3.3 The Detailed Immersion Test

In so far as was possible, the design of the immersion test parallels that of the long-term hydrazine compatibility testing being conducted by JPL (e.g., [4-13]). The purpose of this is to ultimately allow comparison of predictions based on short-term experiments with real-time exposures.

Specimen Coupons - The 6Al-4V titanium was obtained from JPL stock of the material used in their long-term compatibility testing. It was produced by Titanium Metals Corporation of America per MIL-T-9046E, Type III, Composition C, annealed. The titanium was in the form of 0.063 inch sheet and was identified as a portion of heat G-1863. The latter had the following certified analysis:

TABLE 4-11  
CHEMICAL COMPOSITION OF 6Al-4V TITANIUM SPECIMENS

Carbon	0.023%	Vanadium	4.1%
Iron	0.09%	Hydrogen	0.012%
Nitrogen	0.010%	Oxygen	0.10%
Aluminum	5.1%	Titanium	90.565 (by difference)

The specimen configuration selected was essentially a scaled-down version of the slug-type coupons employed in the 110°F (316.5°K) long-term compatibility tests being conducted by JPL [4-13 and 4-20]. Since the experimental approach adopted did not concern itself with behavior in the gas phase, the scaling was based solely on the immersed portion of the JPL coupon. The latter had a metal surface to propellant

volume ratio of approximately  $0.5 \text{ cm}^{-1}$ . Based on the thickness of the furnished material and the propellant volumes attainable in the exposure capsule (see below) a nominal specimen size of  $0.5 \text{ cm} \times 1.9 \text{ cm} \times 0.14 \text{ cm}$  ( $0.20 \text{ in.} \times 0.75 \text{ in.} \times 0.55 \text{ in.}$ ) was selected.

The specimens were machined, cleaned and passivated per JPL specification [4-20 and 4-21], with the exception that isopropyl alcohol was substituted for Freon TF wherever the latter appeared. This was done by direction [4-22] in order to avoid the possibility of chloride contamination which has been experienced elsewhere [4-23]. No identifying marks were placed on the specimens. They were assigned the number of the capsule in which they received their exposure and handling procedures designed so that upon removal from the capsule they were immediately placed into containers which had been prepared and numbered so as to have a one-to-one correspondence with the capsules.

Test Fluid - The hydrazine utilized in fulfillment of Contract NAS7-789 was purchased from the Olin Corporation, Chemical Division, Stamford, Connecticut, per MIL-P-26536C. The material was shipped from Olin's plant at Lake Charles, Louisiana, on 21 August 1972 in Drum No. H-108. The latter container is made of 304L corrosion resistant steel [4-24]. Subsequent transfers were accomplished by pressurization with dry nitrogen to small 321 stainless steel containers which are more convenient to handle in the laboratory. In all such operations, care was taken to prevent exposure of the hydrazine to air. An assay of the material is shown in Table 4-12.

In addition to testing with neat hydrazine, it was felt that the predictive method might be better demonstrated by "doping" the propellant with chloride ion. Presence of the latter is known to accelerate corrosion of titanium [e.g., 4-2, 4-16 and 4-23]. The selection of the amount of chloride to be added (nominally, 5, 25, and 50 ppm by weight) was derived by considering its typical concentration in as-supplied hydrazine (less than 5 ppm) [4-15 and 4-25], the anticipated maximum listed in the proposed Mil Spec (5 ppm) [4-17], and the amount found from residual Freon TF ( $\sim 100 \text{ ppm}$ ) resulting from typical capsule cleaning operations [4-22].



TABLE 4-12

ANALYSIS OF HYDRAZINE, DRUM NO. H-108

<u>Component</u>	<u>Spec. Limits</u>	<u>Assay Value</u>	<u>Analytical Method</u>
Hydrazine, wt. %	98.0 (min.)	98.13	Chloramine T
Water, wt. %	1.5 (max.)	0.5	Gas Chromatography
Titanium, ppm	None	0	Modified atomic
Aluminum, ppm	None	0	Absorption Spectroscopy
Vanadium, ppm	None	0	" "
Iron, ppm	None*	1.3	" "
Chromium, ppm	None	.065	" "
Manganese, ppm	None	.004	" "
Nickel, ppm	None	.161	" "
Chloride, ppm	None*	<1	Turbidimetry

\*A supplemental data sheet to MIL-P-26536C, dated 15 June 1972, suggests that specification limits for iron and chloride should be 20 and 5 ppm, respectively. In addition, the supplement suggests that the limits for the weight percents of hydrazine and water be set to 98.5 (min.) and 0.5 (max.), respectively.

Test Geometry - No restraints were placed on the test geometry other than that the capsule opening must be large enough to admit the specimen, cross section, 0.5 cm x 0.14 cm (nominal), and the inside diameter must be such that introduction of approximately 4 cm<sup>3</sup> of hydrazine would result in complete immersion of the sample. To avoid a continual loss of hydrazine during the course of the experiment, it was required that the capsule be sealed.

Container Design - Consideration of the various requirements placed upon the exposure capsule or container resulted in the selection of commercially available 13 x 100 mm Kimax (chemically equivalent to Pyrex) biological culture tubes. These have an internal volume of ~9 cm<sup>3</sup> and are fitted with screw caps containing a Teflon insert.

The tubes were checked for the integrity of their cap seal by immersing them in 180°F water and observing whether any air bubbles escaped. Those which released bubbles were discarded; the remainder were cleaned per the JPL specifications (for glass) in Reference 4-21. The caps were carefully swabbed out with lintless tissue moistened with isopropyl alcohol. To assure positive identification, serial numbers were placed on the etched surface provided on the glass and were inscribed on the cap with an awl. One of these exposure capsules, together with a 1.9 cm long titanium specimen, is shown in Figure 4-17.

Nine-holed fir blocks were prepared to support the tubes while in the ovens (Figure 4-18). The hole depth was such that the hydrazine liquid level was not visible. Although it was recognized that this configuration retards the rate at which the samples initially reach the equilibrium exposure temperature (the time differential is considered insignificant except for very short exposures), it was felt that this was offset by the inherent safety aspects offered by a solid block in the event of a capsule rupture. The "9-pack" was designed for the convenience of the overall experiment, wherein each withdrawal group was made up of eight metallic specimens and a blank.

Instrumentation - No internal instrumentation was employed in these tests. All data, with the exception of the exposure temperature, was collected through pre and post-test activity. Provision was made for continuous monitoring of the exposure temperature by means of a suitable thermocouple - recorder combination. The ovens utilized proved to be so stable, however, (see below) that sampling frequency was reduced to twice daily.

Test Conditions - There are four distinct test conditions which were required to be established for this set of experiment, viz, time, temperature, metal surface to propellant volume ratio and chloride dopant level. The values selected for each of these parameters will be discussed in turn.



FIGURE 4-17: EXPOSURE CAPSULE AND 6A1-4V TITANIUM SPECIMEN



FIGURE 4-18: ARRAY OF CAPSULES IN THE WOODEN EXPOSURE BLOCK

- (1) Time - Contractual time limitations at the outset of this phase of the program limited the maximum exposure time to approximately 60 days. In the interest of spacing the data evenly on a log time scale, this period was broken into 5 withdrawal times, nominally 3.75, 7.50, 15, 30 and 60 days. To obtain the maximum exposure time, the 60 day specimens were prepared first; the 7.50 day, 15 day and 30 day specimens were then prepared as a group. Because the 3.75 day exposure could be run at almost any time during the test program, and because there was a definite uncertainty as to the reactivity of the system, it was decided to delay preparation of this set until results were obtained from the 7.5 and 15 day exposures. As it turned out, the latter indicated such a low rate of reactivity that a shorter exposure would have proved meaningless; accordingly, the number of withdrawals was reduced to four.
- (2) Temperature - Two exposure temperatures were selected, 316.5°K (110°F) and 344.3°K (160°F). There are a number of theoretical and operational reasons for this selection:
  - (a) They are temperatures of interest in propulsion systems for long-lived spacecraft; as such they are currently being employed by JPL in long-term compatibility tests being conducted on metallic and non-metallic materials in hydrazine [4-13 and 4-16]; their use will permit comparisons of predictions based on this study with real time results from the JPL program.
  - (b) They are sufficiently separated that a rate dependence on temperature should be discernible if any exists.
  - (c) They are operationally convenient in terms of oven control (sufficiently removed from room temperature) and hydrazine vapor pressure (important in a glass system).

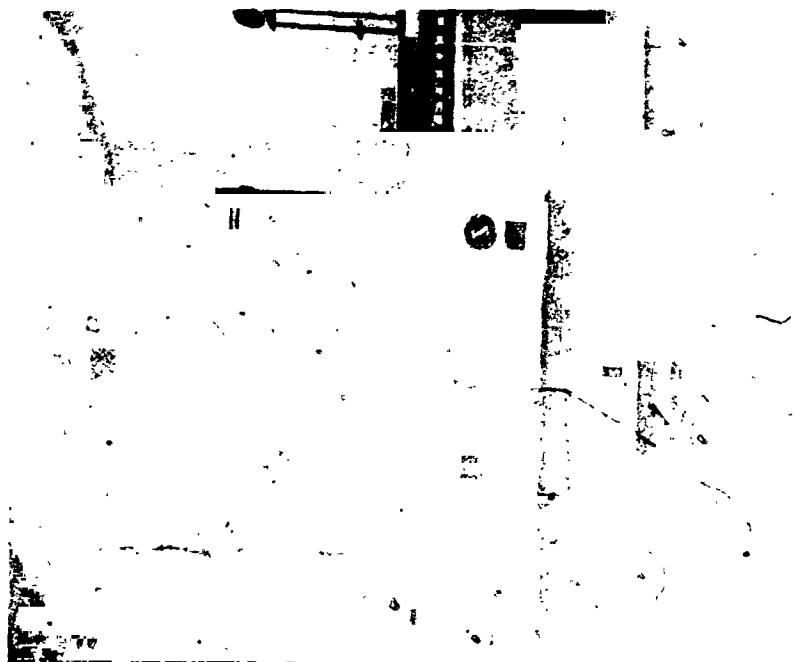


FIGURE 4-19: NITROGEN - PURGED PLASTIC ENCLOSURE  
USED FOR ALL HYDRAZINE TRANSFER OPERATIONS

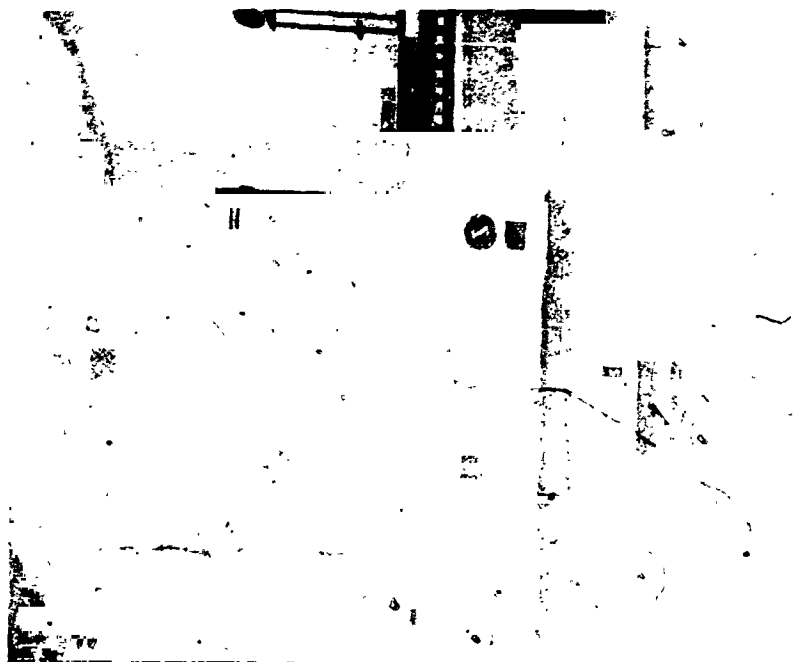


FIGURE 4-20: CONSTANT - TEMPERATURE OVENS AND RECORDER

- (3) Surface to Volume Ratio - As stated earlier, under Specimen Coupons, the nominal surface to volume ratio was set at  $0.5 \text{ cm}^{-1}$  to match the exposure condition of the JPL slugs.
- (4) Chloride Dopant Level - This was also covered previously (under Test Fluid). The values selected (5, 25, and 50 ppm) cover the approximate range (up to 60 ppm) and were operationally convenient in that only a single standard chloride solution was required.

In line with the attempt to demonstrate a simple, modestly-priced procedure, it was decided to run single samples at a larger number of conditions rather than replicates. The combination of two temperatures, four dopant levels and five withdrawal times yielded a total of 40 samples.

Test Setup - The experimental concept for this series of tests is so simple that a description of the "test setup" is superfluous. All required details are contained either in the description of the specimen and container (above) or the test procedure (below).

Test Procedure - The procedure followed was straightforward. The specimens and capsules were cleaned and passivated, as described previously. The capsules were then weighed on a Mettler balance (certified accuracy of  $\pm 0.25 \text{ mg}$ ). Those which were to contain chloride were prepared by pipetting in the appropriate amount of a standard chloride solution and carefully evaporating to dryness. The metallic specimens (which had been kept in a desiccator following cleaning and passivation) were then weighed and placed in the capsules. The latter were pre-flushed with dry nitrogen to remove air. A final flush was accomplished within a small plastic bag, and all subsequent filling operations were conducted in an inert atmosphere provided by the continuous flow of pure, dry nitrogen through a specially designed plastic enclosure (Figure 4-19). All manipulations within this enclosure were conducted by working at its periphery and grasping the various items through the polyethylene film. The hydrazine supply tank (approximately 5 liters) was pressurized to about  $2 \times 10^5 \text{ N/m}^2$  (30 psig) with dry nitrogen and the propellant delivered directly to the capsule via a previously flushed 321 CRES line. This addition was not quantitative, but merely to a pre-

marked line which estimated the 4 cm<sup>3</sup> level selected. The caps were screwed down securely and the capsules were removed from the inert atmosphere and weighed. This provided (by difference from previous weighings of capsules and specimens) an exact determination of the amount of hydrazine charged to each capsule.

The capsules were then sorted into the appropriate "9-pack" and placed in the designated environment (316.5°K or 344.3°K). This environment was provided by Blue M mechanical convection ovens (Figure 4-20) which employ what is termed proportional control. This results in very stable temperatures; over the time of exposure the measured temperature never varied more than  $\pm 2^\circ\text{K}$  (approximately  $\pm 3.5^\circ\text{F}$ ).

At the appropriate times the capsules were withdrawn from the ovens, allowed to cool to room temperature and weighed (to determine hydrazine loss, if any). The capsules were then placed in the plastic enclosure and the volume continuously purged with dry nitrogen as before. After a suitable flushing period, the capsules were opened and the metallic specimens were removed, blotted gently with absorbent tissue, and allowed to sit overnight in the nitrogen atmosphere to "dry". The caps were replaced on the capsules and the latter sent to the laboratory for analysis. After overnight "drying" the metallic specimens were placed in a desiccator for 24 hours, then weighed and sealed into individual pre-prepared plastic bags for storage until they could be inspected microscopically.

#### 4.4.4 Correlation of Metal Buildup to Propellant-Material Reaction

The hydrazine was analyzed for metal content by means of an atomic absorption spectrometer, modified to enhance its sensitivity by the addition of a graphite furnace sample introduction system. The results are presented in Table 4-13; they clearly demonstrate that under the conditions of this experiment, the propellant-material reaction is negligible. Based on these data, it may be confidently predicted that hydrazine with impurity levels equal to or less than those reported in Table 4-12 may be stored in 6Al-4V titanium for periods up to ten years with no detrimental effects. In addition, chloride ion concentrations up to 50 ppm (a factor of 10 greater

than the proposed specification limit) have no apparent effect on the 6Al-4V titanium-hydrazine system. It is important to note that these chloride concentrations were achieved by the addition of a salt, sodium chloride. These results, combined with those reported by Tolbert, et al, [4-23] suggest that it is not the chloride ion as such which is responsible for the corrosion of the titanium alloy, but rather an "active" or acidic chloride which forms the fully-ionized hydrazinium chloride. The relative roles of these two ions in the subsequent attack on 6Al-4V titanium is unknown: whether the presence of chloride ion is required in order for the hydrazinium ion to exhibit corrosive behavior is a subject which requires further elucidation. One thing is eminently clear: if the proposed specification limit (5 ppm) is to guard against corrosive behavior, then the analytical method used must be able to distinguish between "active" and "inactive" chloride. As demonstrated by this work, concentrations up to 50 ppm of the latter have no effect on the system. Unless this critical difference is recognized, a total chloride determination of hydrazine lots containing this species could result in unnecessary rejection. Work by TRW [4-28] indicates that the various chlorides formed are sufficiently soluble in hydrazine that they should pose no problems of precipitation and subsequent flow decay.

Two additional pieces of information were obtained during the course of these experiments. The metal coupons were weighed and microscopically (to 30X) examined before and after exposure. The results of this scrutiny are in full agreement with those obtained on the liquid: no weight changes were observed (all fluctuations were within the certified accuracy of the balance,  $\pm 0.25$  mg) and the specimens appeared optically identical in pre-post examinations.

A comment or two may be in order concerning some of the numerical entries which appear in Table 4-13. Iron was randomly encountered in concentrations up to 0.5 ppm. These were considered to be perturbations around the average blank value of 1.3 ppm; individual results ranged from 1.0 to 1.8 ppm. The value reported for aluminum after 7.9 days at 160°F was considered to be spurious. Contamination is suspected; its source is unknown. It should be noted that under the conditions of the analysis, the detection limit for titanium (the most difficult to detect of those sought) was 0.025 ppm.



TABLE 4-13

## ATOMIC ABSORPTION SPECTROSCOPY RESULTS, 6A1-4V TITANIUM/HYDRAZINE

316.5°K (110°F)

Exposure Time, Days	0 ppm Chloride Added				5 ppm Chloride Added				25 ppm Chloride Added				50 ppm Chloride Added			
	Al	V	Ti	Fe	Al	V	Ti	Fe	Al	V	Ti	Fe	Al	V	Ti	Fe
7.9	+	Ø	Ø	¶	+	Ø	+	¶	+	Ø	+	¶	+	¶	Ø	Ø
15	Ø	Ø	+	482	+	Ø	+	Ø	+	Ø	+	¶	+	Ø	+	282
30	60	Ø	+	¶	60	Ø	+	482	+	Ø	+	282	+	Ø	+	¶
60	+	29	+	Ø	+	+	+	Ø	+	29	+	Ø	+	29	+	Ø

344.3°K (160°F)

Exposure Time, Days	0 ppm Chloride Added				5 ppm Chloride Added				25 ppm Chloride Added				50 ppm Chloride Added			
	Al	V	Ti	Fe	Al	V	Ti	Fe	Al	V	Ti	Fe	Al	V	Ti	Fe
7.9	380	¶	Ø	¶	+	Ø	+	Ø	+	Ø	+	Ø	+	Ø	Ø	Ø
15	Ø	Ø	+	Ø	+	¶	+	Ø	+	¶	+	Ø	+	Ø	+	¶
30	Ø	¶	+	Ø	Ø	Ø	+	Ø	110	¶	+	¶	+	¶	+	482
60	+	+	+	Ø	Ø	+	+	Ø	Ø	+	+	Ø	Ø	+	+	Ø

Note: All concentrations expressed in parts per billion (by weight)

Legend:

Ø Sample - Blank &lt; 0

¶ Sample - Blank &lt; Error

+ None Detected

#### 4.5 THE 304L CRES/HYDRAZINE SYSTEM

##### 4.5.1 System Definition and Application

The rationale for the use of hydrazine in long-life spacecraft application has been adequately discussed in Section 4.4.1 and need not be reiterated here. The propellant has been selected for use, but the choice of materials for its containment (whether quiescent or flowing) has not yet been finalized.

One of the more promising corrosion resistant steel (CRES) alloys for hydrazine tankage is designated 304L. This material has the following nominal composition: 64.8% iron, 0.03% carbon (max.), 2.0% manganese, 0.05% phosphorus, 0.03% sulfur, 1.0% silicon, 20.0% chromium, and 12.0% nickel. The L designation refers to the low carbon content; 304 CRES is specified to have a maximum carbon content of 0.08%. It has been shown that reduction of carbon content results in an increased resistance to intergranular corrosion [4-16].

The 304L CRES/hydrazine system has been given at least a provisional compatibility rating. Coulbert and Yankura [4-16] state that the alloy, when immersed in propellant grade hydrazine, exhibits much less than 1 mil/yr. surface erosion. This, together with the fact that it did not promote propellant decomposition or render it impact sensitive resulted in the Defense Metals Information Center assigning 304 CRES a Class 1 (excellent) rating up to 140°F [4-27]. Uney and Fester [4-2], despite the fact that their ratings are based on "non-contaminated hydrazine, i.e., Cl<sub>2</sub> or CO<sub>2</sub> contaminants", give the 304 CRES/hydrazine system a rating of "probable compatibility for short term use (less than six months)" and "doubtful compatibility" for longer periods. No temperature limitations are specified. Lono and Bjorklund [4-13] give 304L an "acceptable" rating for TOPS with a "restricted" qualifier. The latter indicates a temperature limitation, as well as incomplete data.

The 304L CRES/hydrazine system seemed an excellent choice for this study for a number of reasons, some of which are implied in the discussion above. Specifically, they may be enumerated as follows: (1) 304L is probably the most promising CRES for long-life hydrazine systems; (2) the published uncertainties regarding its long term and/or high temperature problems have never been satisfactorily resolved; (3) current consensus, based on such experimental results as those of TRW [4-28] and Rocket Research [4-29], is that the corrosion rate in this system is a function of its carbon dioxide content; and (4) systematic studies of the corrosion rate in this system as a function of carbon dioxide content would both elucidate the system itself and afford a better opportunity (because of higher rates) for verification of the prediction method.

#### 4.5.2 Preliminary Exposure Test

Because of the extensive data which has been generated on this system, some of which has been cited above, there was no necessity to conduct this step and it was bypassed.

#### 4.5.3 Determination of the Rate of Metal Buildup in the 304L CRES/Hydrazine System

##### 4.5.3.1 Selection of the Measurement Technique

Reference to the logic diagram (Figure 2-4) indicates that the method of choice for 304L CRES is the radioactive tracer technique (both iron and chromium furnish suitable, long-lived radiotracers). Due to a number of operational considerations, however, as well as a desire to develop data directly comparable to that being generated by JPL, it was decided to utilize the modified atomic absorption spectroscopy technique for this series of experiments. Specific operational considerations included: (1) 304L CRES foil could not be made available within the required time period; (2) the 304L CRES sheet furnished by JPL (out of the same material lot as their long-term compatibility specimens) was of such a

heavy gauge that activation of specimens fabricated therefrom would have resulted in an inconveniently high radiation level; this would have required the establishment of a series of special procedures; and (3) it was more cost effective to conduct the 304L/hydrazine studies side-by-side with the 6Al-4V titanium/hydrazine studies discussed in Section 4.4. Neither manpower nor funds were available to conduct separate efforts.

#### 4.5.3.2 Selection of the Test Apparatus and Configuration

All considerations for the 304L CRES/hydrazine system are identical to those discussed in Section 4.4.3.2 for the 6Al-4V titanium/hydrazine system; the minimal requirements of the test were satisfied, as before, by use of Kimax glass biological culture tubes.

#### 4.5.3.3 The Detailed Immersion Test

Specimen Coupons - As mentioned above, the 304L CRES utilized in this set of experiments was furnished by JPL, having been selected from the identical material lot as that used for the latter's long-term compatibility testing. It was produced by the Earle M. Jorgensen Company, under Federal Specification QQ-S-766C, covering type 304 low carbon, finished sheet. The material, identified as heat number M-33766, was in the form of 16 gauge (0.0625 in., 1.6 mm) sheet and was accompanied by the certified [4-30] analysis shown in Table 4-14.

TABLE 4-14  
CHEMICAL COMPOSITION OF 304L CRES SPECIMENS

Carbon	0.02%	Nickel	10.80%
Manganese	1.50%	Chromium	18.70%
Phosphorus	0.021%	Copper	0.07%
Sulfur	0.010%	Molybdenum	0.04%
Silicon	0.59%	Iron	68.24% (by difference)

All statements made in Section 4.4.3.3 concerning the configuration and preparation of the 6Al-4V titanium specimens hold equally well for the 304L specimens (realizing, of course, that there are differences in the cleaning and passivation of the two alloys, as detailed in References 4-20 and 4-21).

Test Fluid - Here again, the statements made in Section 4.4.3.3 concerning the hydrazine utilized in that series of tests also apply here. In order to establish the baseline concentrations of the various constituents, an assay was performed per MIL-P-26536C, supplemented by trace element analysis using the modified atomic absorption technique. The results were recorded in Table 4-12.

As in the case of the chloride added to the 6Al-4V titanium/hydrazine system, the 304L CRES/hydrazine system was "doped" with an impurity known to accelerate corrosion; i.e., carbon dioxide. The experimental work which demonstrated this effect has been referenced above. Based on conversation with JPL [4-31], the range of interest was established to be between 5 and 100 ppm carbon dioxide (~5-10 ppm cited as a typical "as supplied" level and up to ~100 ppm for samples which had been exposed to air a number of times with no particular precaution taken to protect them). An assumption was made that the stock hydrazine contained 5 ppm  $\text{CO}_2$ , and "standard" solutions of  $\text{CO}_2$  in hydrazine were prepared at nominal\* levels of 15, 55 and 95 ppm to yield (assumed) nominal totals of 20, 60 and 100 ppm. These solutions were prepared by placing neat hydrazine in specially cleaned septum-equipped bottles and adding the appropriate amounts of gaseous carbon dioxide with a hypodermic needle and precision micro-syringe. The gaseous carbon dioxide was prepared by placing excess "dry ice" in a similar septum-equipped bottle (Figure 4-21) and, with the stopper loosened, allowing the material to sublime and displace

---

\*The actual amounts of carbon dioxide added to these "standard" solutions were 13.5, 43.4 and 85.6 ppm.

the air. As the last trace of solid disappeared, the septum stopper was firmly inserted and the bottle allowed to stand until it was assured that the contents were at room temperature. The last two operations (stopper insertion and warming of the gaseous carbon dioxide) undoubtedly raised the gas pressure within the bottle (  $\sim 35 \text{ cm}^3$  volume) slightly above atmospheric. Approximate calculations indicated that there was a negligible effect on the amounts of carbon dioxide withdrawn.

The situation with respect to the carbon dioxide concentration in as-received hydrazine requires some discussion, as does its variation with time (increase due to exposure to the atmosphere, decrease due to various possible reactions). Uncertainties concerning those concentrations are compounded by the fact that there is apparently no clear cut, straightforward analysis available for the determination of carbon dioxide in hydrazine. This last point will be discussed first; we will then return to the question of  $\text{CO}_2$  concentration as a function of time.



FIGURE 4-21: EQUIPMENT FOR THE PREPARATION OF  $\text{CO}_2$  - DOPED HYDRAZINE

There are currently extant at least four different methods for the determination of carbon dioxide in hydrazine. It is beyond the scope of this report to outline them in detail or to comment on them extensively. A thumbnail description and commentary is presented here only to indicate the extent of the problem.

(1) Dielectric Constant - This method, proposed by Aerojet [4-32], is based upon the premise that the presence of small quantities of ion-producing impurities (such as  $\text{CO}_2$ ) cause a marked increase in dielectric constant. Measurements made with a chemical oscilloscope at 5 MHz indicated that a workable relationship between  $\text{CO}_2$  content and dielectric constant did, indeed, exist. As pointed out by Axworthy, et al [4-35], however, the actual dielectric constant of hydrazine is not changed by the addition of small amounts of impurities; there is an apparent change, though, due to a change in conductivity. Attempts were made during the course of these studies to make meaningful resistance/capacitance measurements of  $\text{CO}_2$  - doped hydrazine employing an impedance bridge. The observations of Axworthy were confirmed: the capacitance of the impedance cell (dielectric constant) was insensitive to  $\text{CO}_2$  content but the resistance of the cell (conductivity) was significantly altered by as little as 15 ppm  $\text{CO}_2$  added. A useful interpretation of the results proved elusive, however, due to the complex (and largely unknown) chemistry of the system as well as a lack of information concerning the relationship between the measurements and the impurities other than  $\text{CO}_2$  such as  $\text{H}_2\text{O}$  and aniline, all of which contribute to the conductivity. The method is considered unreliable until further elucidation of the fundamental relationships is obtained.

(2) Sulfamic Acid/Gas Chromatography - This method, developed by Vango at JPL [4-33], involves the addition of hydrazine to an excess of sulfamic acid. This liberates the carbon dioxide, which is swept from the solution by helium gas, passed through concentrated sulfuric acid (to absorb entrained water) and trapped on glass beads at liquid nitrogen temperature. This isolated material is then analyzed by means of a suitable gas chromatographic procedure.

The method is classical and straightforward, although somewhat time consuming. There is no question but that it determines the  $\text{CO}_2$  content of the hydrazine. The difficulty in application arises from the fact that it liberates all the carbon dioxide contained in the hydrazine. As discussed below, this is only a portion of the information required to assure behavior compatible with long-life operation.

(3) Dual Column Chromatography - This is the method utilized by Christopher and Brown in conducting their survey of typical hydrazine contamination [4-15]. Samples are introduced to the gas chromatograph with no pretreatment. Elution times and peak heights are first obtained using assayed hydrazine. Standards are then prepared by adding weighed amounts of each impurity to weighed hydrazine samples and then extrapolating the results to determine the original amounts of these constituents (e.g.,  $\text{CO}_2$ ) in the hydrazine by calculating peak height ratios.

This method is subject to question for a number of reasons:

(1) as mentioned previously, the basic chemistry involved in this system is largely unknown. The multitude of reactions which could be occurring in  $110^\circ\text{C}$  columns packed with a variety of materials cannot be expected to simplify this chemistry. To assume that the  $\text{CO}_2$  is liberated quantitatively seems optimistic; (2) the ability to separate the ammonia and the  $\text{CO}_2$  peaks is difficult, at best. In a complex column at  $110^\circ\text{C}$ , with detector and inlet temperatures of  $150^\circ\text{C}$ , it is possible to obtain sufficient ammonia to completely mask the carbon dioxide; (3) there is no reported attempt to verify results by running, e.g., an ultrapure hydrazine to demonstrate the absence of a peak in a  $\text{CO}_2$ -free system; and (4) the  $\text{CO}_2$  results obtained in this study seem anomalously high. This will be discussed below.

(4) Iron Dissolution - This method is employed by Rocket Research Corporation [4-34] in assaying incoming hydrazine. The procedure is simple: 1 gram of iron powder is contacted with 20 ml of hydrazine at  $25^\circ\text{C}$  ( $77^\circ\text{F}$ ) for 30 minutes. The dissolved iron is then determined by standard laboratory techniques.



There are two attractive features to this method: (1) it is rapid; and (2) it measures the "reactive" carbon dioxide present; any  $\text{CO}_2$  tied up in compounds will not be detected. This latter point will be discussed below; the fact that other corrosive contaminants (such as hydrazinium chloride) may be lumped with  $\text{CO}_2$  as a result of this analysis is not necessarily detrimental. An operational limitation exists; however, while it is relatively easy to determine whether or not a drum of hydrazine has a  $\text{CO}_2$  content at or near 200 ppm, the more typical levels (5-10 ppm) would yield such low iron concentrations that they would probably be obscured by the background or noise level of any analysis used.

The question "What is the  $\text{CO}_2$  content of as-received hydrazine, and how does it vary with time?" is obviously not a simple one. The chemistry which is going on at the ppm concentration levels is significant in the planned applications of this system; its complexity is indicated by the analytical problems and discrepancies which have arisen therefrom. JPL, using Vango's method, reports that as-received hydrazine contains 5-10 ppm  $\text{CO}_2$  and that the level can rise to the vicinity of 100 ppm if no particular precautions are taken during the handling of the material (e.g., a drum used as a supply for various small requirements over the period of a year or so). Rocketdyne, utilizing a  $\text{CO}_2$  liberation/chromatographic method somewhat similar to that of Vango, reports ~60 ppm  $\text{CO}_2$  in RPL-purified hydrazine [4-35]. Aerojet indicates that tank car hydrazine contains less than 10 ppm  $\text{CO}_2$ , as measured by the dielectric constant method. Rocket Research, employing the iron dissolution method on 17 hydrazine samples, reports iron concentrations equivalent to 10 ppm  $\text{CO}_2$  or less [4-34]. By plotting average metal content vs  $\text{CO}_2$  dopant level for the 60-day exposures in the current research (which amounts to a long-term, high temperature version of the Rocket Research iron dissolution method), the  $\text{CO}_2$  content of the Boeing hydrazine supply is estimated to be less than 3 ppm.

The foregoing results are in general agreement, and all fall below the 100 ppm level. On the other hand, the most recent investigation is in sharp disagreement. United Aircraft Research Laboratories, employing the dual column chromatographic method on 24 hydrazine samples gathered from 12 users, reports [4-15]  $\text{CO}_2$  levels from 0.1% to 0.6% (1000 to 6000 ppm). While no histories are available on the individual drums, it seems

logical to assume that the exposure of their contents to air runs the full gamut from complete exclusion to no protection whatsoever. Considering this, the reported  $\text{CO}_2$  contents are surprisingly high.

This discrepancy suggests that further study may be required prior to the assignment of a meaningful specification limit. A consensus must be obtained not only on the analytical method for determination of carbon dioxide, but also on the relationship between the  $\text{CO}_2$  content and the onset of detrimental effects to the system. It is a conclusion of this program that the carbon dioxide dissolved in hydrazine exists in two states, labile and non-labile (i.e. reactive and non-reactive). In the former case, it is in the form of fully ionized hydrazinium carbazate, and capable of removing metal atoms from the container walls by chemical reaction with the formation of a metal carbazate salt. This reaction is analogous to the action of a strong mineral acid on a metal with the subsequent formation of the metal salt. A logical conclusion is that old hydrazine (assuming no further exposure to the atmosphere) should be less corrosive than new, all the labile carbazate having reacted in the process. If the original  $\text{CO}_2$  content is sufficiently high, it is possible that these reaction products, although non-corrosive, could agglomerate and give rise to another problem: flow decay.

Thus it would appear that two different  $\text{CO}_2$  determinations should be performed on each drum (or tank car). One would analyze for total carbon dioxide, which would be a measure of flow decay potential; the other would determine the labile or active carbon dioxide, which would be a measure of corrosion potential. Of the four methods currently in use, only the iron dissolution method of Rocket Research appears suitable for determination of the labile  $\text{CO}_2$  and its sensitivity at low  $\text{CO}_2$  contents has already been discussed. Further work on analytical methods is clearly indicated. Although Rocketdyne reported on inability to reduce the carbazic acid content of hydrazine below 0.02% treatment with barium oxide [4-35], the concept of chemical pretreatment followed by filtration through molecular sieves [4-36] appears to be an attractive

method for assurance of hydrazine propulsion system stability and long life. Other methods for the refinement of hydrazine have also been studied by JPL [4-13].

Test Geometry - All considerations and decisions made with regard to this parameter, as well as the subsequent items of container design, instrumentation, test conditions, test setup, test procedure and post-test measurements, are identical to those discussed for the 6Al-4V titanium system (Section 4.4.3) with the following exceptions (all related to the difference in dopant material):

(1) The dopant used in the 304L CRES/hydrazine series of tests was carbon dioxide, added (as described previously) to yield nominal levels of 20, 60, and 100 ppm.

(2) Rather than adding the dopant and the hydrazine to the test capsule separately, stock solutions of the hydrazine with dopant ( $\text{CO}_2$ ) were made up under an inert atmosphere in the special plastic enclosure described previously. Aliquots (four  $\text{cm}^3$ ) of these solutions were then transferred to the appropriate capsules (which had been weighed and equipped with weighed 304L CRES coupons) by means of bulb syringes which had received the same special cleaning as the septum bottles containing the stock solutions (essentially an abbreviated version of the JPL standard procedure [4-21]). The entire capsule assembly is then weighed and the exact amount of hydrazine determined by difference.

(3) The post-test atomic absorption analyses were complicated by the fact that a precipitate developed in those capsules which contained  $\text{CO}_2$ -doped hydrazine. Following removal of the 304L CRES coupons, the capsules were centrifuged and the hydrazine drawn off (with specially cleaned bulb syringes, a new one for each sample) for analysis, as before. The precipitate was then dried (by careful evaporation) and dissolved in hydrochloric acid. The resulting solution was evaporated, the residue again taken up in  $\text{HCl}$ , re-evaporated and finally dissolved in a measured amount of distilled, deionized water. Aliquots were drawn from the latter for atomic absorption analysis.

#### 4.5.4 Correlation of Metal Buildup to Propellant-Material Reactions

A compilation of the atomic absorption spectroscopy test results is presented in Table 4-15. Net increase in metals are reported in all cases, and, where a precipitate was formed, analyses were conducted on both phases (as discussed previously) and total increase in metal contents reported. There was essentially no change in the level of metals found in the blanks throughout the course of the experiment. As a result, the average of all of these results was used in establishing the blank correction to be applied to the individual analyses. The availability of a larger population allowed a limited statistical treatment; the derived results were as follows: chromium:  $65 \pm 15$  ppb; iron:  $1318 \pm 216$  ppb; manganese:  $4 \pm 1$  ppb; nickel:  $161 \pm 43$  ppb. It should be noted that these standard deviation (which are considered to arise from errors in the analysis - see Section 3.3) average approximately 23% of the mean value. This, together with uncertainties in the true surface area of the individual specimens, as well as the thickness of their passivation layers, could easily result in a total error of 50% in the reported results.

A review of the data in Table 4-15 reveals a number of anomalies, e.g., unexpected reversals as a function of time and temperature. Considering the fact that each value reported in the matrix represents a single specimen, however, and is subject to errors of the magnitude described above, it is felt that the results are quite well-behaved. Combining them with other experimental observations allowed the following conclusions to be drawn:

- (1) The kinetics of the corrosion process are very weak functions of the temperature, if at all, within the range studied.
- (2) The undoped hydrazine (estimated to have less than 3 ppm  $\text{CO}_2$  by extrapolation of the data from these tests) exhibits complete compatibility with 304L CRES under

TABLE 4-15

## ATOMIC ABSORPTION SPECTROSCOPY RESULTS, 304L CRES/HYDRAZINE

316.5°K (110°F)

Exposure Time, Days	0 ppm CO <sub>2</sub> Added				13.5 ppm CO <sub>2</sub> Added				49.4 ppm CO <sub>2</sub> Added				85.6 ppm CO <sub>2</sub> Added			
	Cr	Fe	Mn	Ni	Cr	Fe	Mn	Ni	Cr	Fe	Mn	Ni	Cr	Fe	Mn	Ni
7.9	Ø	Ø	Ø	Ø	82	359	22	71	90	356	14	53	114	638	22	111
15	22	†	Ø	†	229	1246	32	190	98	735	21	97	151	774	24	121
30	52	Ø	Ø	†	153	931	30	157	140	1050	23	150	185	691	18	150
60	†	Ø	Ø	Ø	689	2039	50	255	4126	12752	188	1302	6336	20209	304	2000

344.3°K (160°F)

Exposure Time, Days	0 ppm CO <sub>2</sub> Added				13.5 ppm CO <sub>2</sub> Added				49.4 ppm CO <sub>2</sub> Added				85.6 ppm CO <sub>2</sub> Added			
	Cr	Fe	Mn	Ni	Cr	Fe	Mn	Ni	Cr	Fe	Mn	Ni	Cr	Fe	Mn	Ni
7.9	Ø	Ø	+	Ø	52	472	27	83	118	418	19	166	162	473	22	183
15	†	†	+	†	187	978	28	170	113	663	22	151	262	878	22	165
30	†	†	†	60	147	1046	31	157	165	1062	18	158	700	2017	45	319
60	Ø	Ø	Ø	†	171	1306	20	131	4530	15192	250	1854	3868	12729	181	1509

Note: All concentrations expressed in parts per billion (by weight) and have been normalized to an average S/V of 0.69 cm<sup>-1</sup>.

Legend:

Ø Sample - Blank &lt; 0

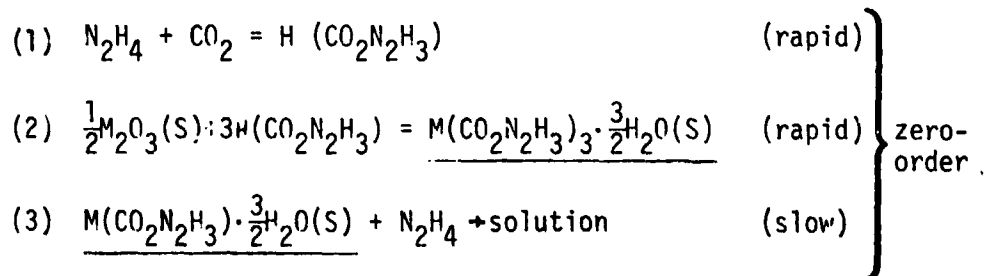
† Sample - Blank &lt; Error

+ None Detected

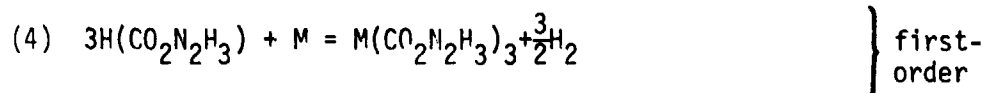
the conditions of this test. There is essentially a zero metal buildup; no precipitate formed in any capsule containing undoped hydrazine. These results allow confident prediction that hydrazine with impurity levels equal to or less than those found in Drum No. P-108 can be stored in 304L CRES containers at temperatures below 134°F for periods up to ten years with no deleterious effect.

- (3) The buildup of metal in the doped hydrazine (including that in the precipitate) is roughly linear for the first 30 days of exposure, and was essentially unaffected by variations in  $\text{CO}_2$  content between 13.5 and 86.6 ppm.
- (4) After 30 days, the rate of metal buildup is greatly accelerated and is a strong function of the  $\text{CO}_2$  content.

Conclusions (3) and (4) strongly suggest that the corrosion of 304L CRES in these solutions is pseudo-zero order for the first 30 days and first order with respect to  $\text{CO}_2$  beyond that time. A possible explanation for such behavior is related to the slow dissolution of the metal oxide layer (formed by the passivation process) by the carbazic acid (or, more exactly named, hydrazinium carbazate) which results from the reaction between  $\text{CO}_2$  and hydrazine. One example of such a mechanism is:



to be followed by



The zero-order reaction is predicted to be independent of the  $\text{CO}_2$  concentration because the rate is controlled by the slow step, (3). The rate of the latter should be a function of the exposed surface and the volume of the oxide coat. It should be emphasized that no actual data have been gathered to verify the foregoing sequence; it is purely hypothetical and meant to represent only a possible type of mechanism. The general validity of the hypothesis is strengthened, however, by means of calculations based on some assumptions concerning specimen surface roughness and the thickness of the oxide layer. Uhlig and Lord [4-37] have studied the properties of an oxide layer formed on 18-8 stainless steel as a result of surface treatment ("pickling", or passivation) by various acids. They report an oxide thickness of 17 Å and surface roughness factors (true area/apparent area) that are as high as 4.1, depending upon the passivation treatment. Accepting the 17 Å thickness and selecting a surface roughness factor of 4 as being representative of the results of passivating the hand-lapped specimens utilized in these experiments, allows the calculation of the amount of iron which would be contained in the oxide layer.

The average specimen has dimensions of 0.14 X 0.5 X 1.9 cm. This yields an apparent surface area of 2.57 cm<sup>2</sup>. Applying the surface roughness factor of 4 yields a "true" surface area of 10.28 cm<sup>2</sup>. Multiplication of this area by the 17 X 10<sup>-8</sup> cm thickness gives an oxide volume of 1.75 X 10<sup>-6</sup> cm<sup>3</sup>.

Assuming that both  $\text{Fe}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  are represented by a model compound of molecular weight 160 and density of 5.24 grams/cm<sup>3</sup>, the volume occupied by a metal atom in the oxide layer can be calculated as

$$\frac{160 \text{ grams}}{\text{mole}} \times \frac{1 \text{ cm}^3}{5.24 \text{ grams}} \times \frac{1 \text{ mole}}{6.02 \times 10^{23} \text{ molecules}} \times \frac{1 \text{ molecule}}{2 \text{ metal atoms}} = \frac{2.53 \times 10^{-23} \text{ cm}^3}{\text{metal atom}}$$

Combination of these results with the percent iron in 304L CRES yields:

$$1.75 \times 10^{-6} \text{ cm}^3 \times \frac{1 \text{ metal atom}}{2.53 \times 10^{-23} \text{ cm}^3} \times \frac{.6825 \text{ iron atoms}}{1 \text{ metal atom}} = 4.36 \times 10^{-6} \text{ grams iron}$$

The average volume of hydrazine in a test capsule is  $3.75 \text{ cm}^3$ ; assuming a hydrazine density of  $1 \text{ g/cm}^3$ , the iron content in the oxide layer, when fully dissolved, would have a concentration of  $4.36 \times 10^{-6} / 3.75 = 1.16$  parts per million. This is to be compared with the average (since it is assumed there is no temperature dependence) iron content of 1.13 parts per million. The agreement is excellent, and while surface roughness factors from 1 to 6 and oxide thicknesses as high as  $100 \text{ \AA}$  have been reported [4-38], the foregoing calculations strongly support the feasibility of the mechanism. The theory then predicts that the concentration of iron during the first 30 days follows the relationship:

$$\text{Fe}_{\text{ppm}} = 0.0387 t_{\text{days}} \quad (\text{apparent } S/V = 0.69 \text{ cm}^{-1})$$

The theoretical line, together with the experimental points, is presented in Figure 4-22. It should be noted that lines for the other metals could be derived in the same manner. In general, they would be found to be related to the iron results, since, in both solution and precipitate, the percentages of the metals determined were in close agreement with those in the original alloy.

Examination of the 60-day data indicates it is best fit by considering the reaction to be temperature-independent, first-order with respect to  $\text{CO}_2$  and possessing a half-life of 16 days. This corresponds to the relationship:

$$-\frac{d}{dt} [\text{CO}_2] = (0.0433/\text{day}) [\text{CO}_2 \text{ ppm}]$$

or logarithmically:

$$\ln \frac{[\text{CO}_2 \text{ ppm, init.} - 4.05]}{[\text{CO}_2 \text{ ppm, } t=t_2]} = (0.0433/\text{day}) \cdot t_2$$

Where  $t_2$  is the number of days elapsed after 30 (i.e., following dissolution of the oxide coat) and 4.05 is the amount of  $\text{CO}_2$  which is depleted in removing



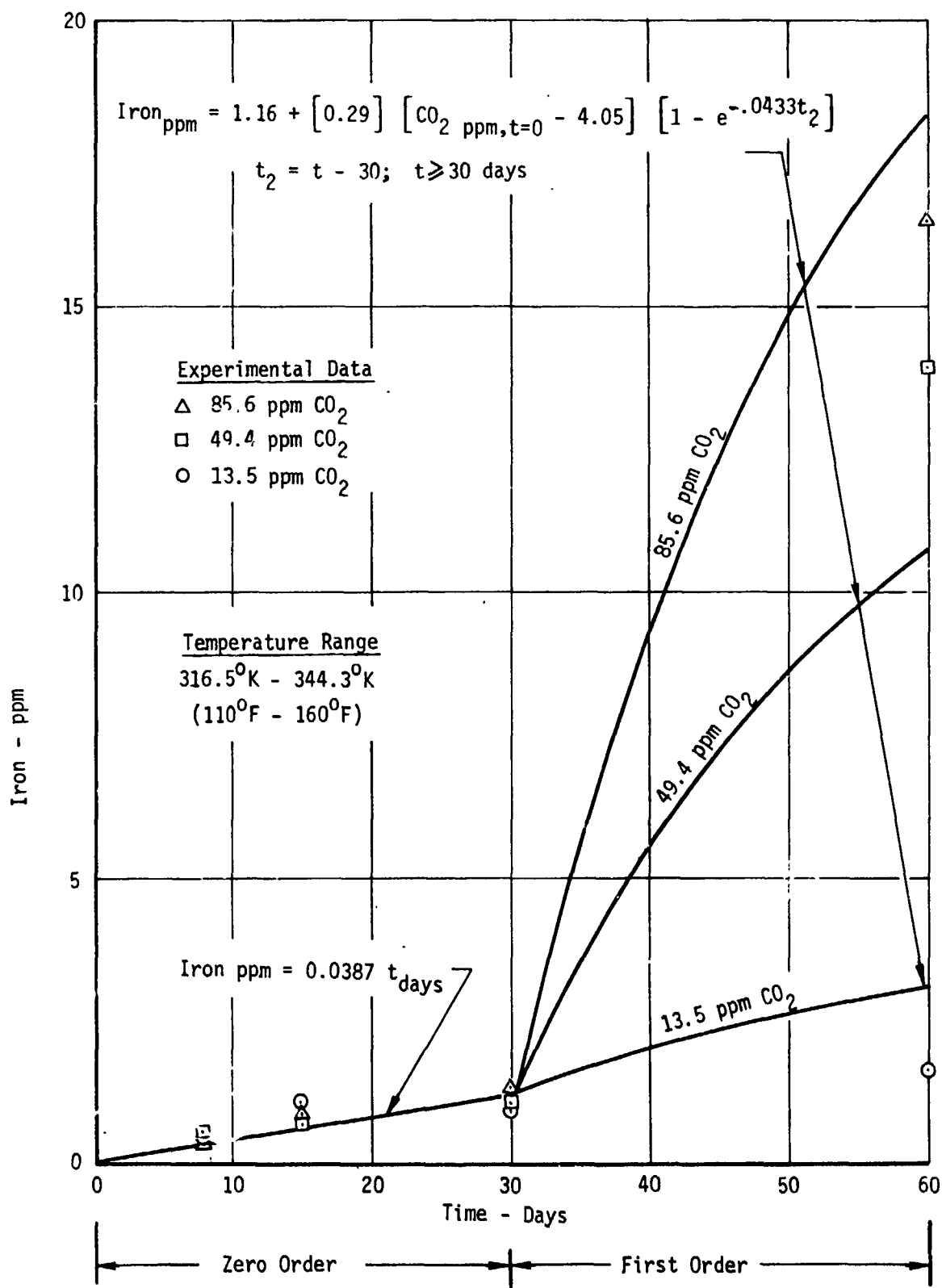
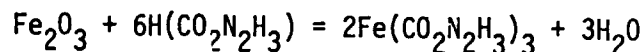


FIGURE 4-22: COMPARISON BETWEEN THEORETICAL AND EXPERIMENTAL BUILDUP OF IRON IN THE 304L CRES/HYDRAZINE SYSTEM ( $S/V = 0.69 \text{ cm}^{-1}$ )

the oxide coat. It is assumed that three moles of  $\text{CO}_2$  combine with each gram-atom of metal, e.g.,



By utilizing the ratios of combining molecular weights, the percent iron in 304L CRES, and assuming the molecular weight of iron is representative of the metal atoms in 304L, a relationship between the ppm  $\text{CO}_2$  reacted and ppm iron dissolved may be derived:

$$\text{ppm } \text{CO}_2 \text{ reacted} = \frac{44 \text{ g}}{\text{mole } \text{CO}_2} \times \frac{\text{mole Fe}}{55.8} \times \frac{3 \text{ moles } \text{CO}_2}{\text{mole Fe}} \times \frac{\text{g metal}}{.6825 \text{ g Fe}} (\text{ppm Fe dissolved})$$

$$\text{ppm } \text{CO}_2 \text{ reacted} = 3.47 (\text{ppm Fe dissolved})$$

This result can be used to derive a kinetic expression for the rate of buildup of iron (other metals are proportional, as before) after the initial 30-day period:

$$[\text{CO}_2]_{t=t_2} = [\text{CO}_2]_{t_2=0} (e^{-kt_2})$$

$$[\text{CO}_2]_{\text{reacted to time } t_2} = [\text{CO}_2]_{t_2=0} - [\text{CO}_2]_{t_2=0} (e^{-kt_2})$$

$$\text{but } [\text{CO}_2]_{\text{reacted to time } t_2} = 3.47 [\text{Fe}_{\text{ppm}}] \text{ dissolved}$$

$$\text{thus } [\text{Fe}_{\text{ppm}}]_{\text{dissolved}} = (0.29) [\text{CO}_2]_{t_2=0} (1 - e^{-kt_2})$$

and the total iron buildup is the sum of the zero-order (phase 1) and first-order (phase 2) equations:

$$\text{Fe}_{\text{ppm}} = 0.0387t_1 + (0.29) [(\text{CO}_2 \text{ ppm})_{t_1=0} - 4.05] [1 - e^{-.0433t_2}]$$

where:  $t_1$  has a maximum value of 30 days and  $t_2 = t - 30$ , where  $t \geq 30$  days.

The theoretical lines (one for each CO<sub>2</sub> dopant level) are presented in Figure 4-22, together with the 60-day experimental measurements. The agreement is satisfactory, considering that a data point represents a single specimen, and variations in surface area and analytical errors can readily account for the discrepancies between the theoretical and measured results.

Pre- and post-test weighing and microscopic examination of the metallic specimens yielded results very similar to those obtained with the 6Al-4V titanium. Weight changes were within the uncertainty band ( $\pm 0.25$  mg) of the balance. Viewing at 30X indicated nothing of interest beyond very faint "water spots" on some of the specimens. No traces were found of the precipitate observed in the capsules; it is apparently non-adherent to the 304L.

As in almost any experiment, additional data would be beneficial. These could consist of replicates of previous conditions; such results would reduce the uncertainties due to the various errors, etc., mentioned previously. It would be more "important", however, to conduct tests at longer exposures in an attempt to verify the hypothesized leveling of the metal concentration vs time curve as the CO<sub>2</sub> is depleted. Proof that the CO<sub>2</sub> is not regenerated and thus limited in its corrosion potential could be very reassuring. Finally, the composition and characteristics of the precipitate (which appeared in every 304L CRES capsule which was charged with CO<sub>2</sub>-doped hydrazine) requires elucidation. It forms within 24 hours of the initial exposure, is olive green when fresh (Figure 4-23) and darkens to a yellowish-brown with age. It is somewhat more finely-ground in the capsules exposed at the lower temperature; the amount seems somewhat greater (visually) at the higher temperatures, but this may be due to the greater "fluffiness" of the precipitate under these conditions. The amount does not seem to change (visually) after the first few days. Nothing is known about the makeup of these precipitates, other than that they contain

REPRODUCIBILITY OF THE ORIGINAL PAGE IS POOR,



FIGURE 4-23: PRECIPITATE FORMATION IN THE 304L CRES/HYDRAZINE SYSTEM  
DOPED WITH 85.6 PPM CO<sub>2</sub> AND HELD AT 344.3°K (160°F)

metal ions in about the same ratios as in the original alloy. The concern, of course, is whether they could achieve sufficient concentration to result in flow decay.

Despite the lack of data pointed out in the previous paragraph, this study has yielded significant results. In addition to the conclusions listed earlier in this section, the following statements may be made:

- (1) The prediction method has been verified by use of sensitive techniques in a simple, straightforward experiment.
- (2) The work has resulted in the establishment of the first quantitative relationships between corrosion rate and typical  $\text{CO}_2$  content in the 304L CRES/hydrazine system. All previous work used unreasonably high  $\text{CO}_2$  content in attempting to accelerate the effects.
- (3) In addition to the earlier conclusion that there was no 304L CRES corrosion in the absence of added  $\text{CO}_2$  (in the specific drum of hydrazine employed), it is also indicated that  $\text{CO}_2$  levels less than 4 ppm can be tolerated, since they would be insufficient to dissolve the entire protective oxide coat, if the apparent S/V is not less than  $0.69 \text{ cm}^{-1}$ .
- (4) The appearance of a precipitate in the 304L CRES/hydrazine system doped with 13.5 to 85.6 ppm  $\text{CO}_2$  lends weight to the conclusion that " $\text{CO}_2$ " may be present in two states, labile and non-labile. This indicates that the upper limit to allowable  $\text{CO}_2$  content in the hydrazine may be much lower than previously thought.

#### 4.6 MONOMETHYLHYDRAZINE STUDIES

Because of a continuing interest in the use of monomethylhydrazine as a fuel in spacecraft propulsion systems, a limited number of 5A1-4V titanium and 304L CRES specimens were exposed to this material under temperature/time conditions and surface-to-volume ratios which were identical to those utilized in the hydrazine studies described in Sections 4.4 and 4.5. Budget limitations restricted the study to a minimum: one capsule was prepared for each metal at each temperature and withdrawal period, a total of twenty in all. Only sixteen of these were actually utilized; the shortest exposure (3.25 days) was cancelled because the results of longer exposures indicated little or no corrosion was taking place. In keeping with the extremely narrow scope of this effort, the format of the previous two sections will not be followed; the test description and results will be reported in narrative form.

The specimen configuration, capsules, cleaning and passivation procedures and pre and post-test observations and analyses were identical to those utilized in the hydrazine work. Since no dopant was used, the MMH-exposed specimens are to be compared with those exposed to neat hydrazine.

The monomethylhydrazine was obtained from Boeing stock and met the requirements of MIL-P-27404. The results of the original assay were not made available; no subsequent assay was accomplished. It was noted; upon filling the capsules, that the MMH had a very faint yellowish tint to it. The cause of this discoloration is unknown.

The MMH-filled capsules were withdrawn and the metallic specimens removed, dried, desiccated and weighed in the same manner as their hydrazine counterparts. Post-test weighing revealed no fluctuations outside of the certified accuracy of the balance ( $\pm 0.25$  mg); microscopic examination at 30X indicated no detectable differences in appearance. The results of the atomic absorption spectrographic analyses are presented in Table 4-16. The results of the 7.9-day exposure seem anomalously high;

TABLE 4-16  
MONOMETHYLHYDRAZINE EXPOSURE SUMMARY  
6Al-4V Titanium

Exposure Time, Days	316.5°K(110°F)				344.3°K(160°F)			
	Al	V	Ti	Fe	Al	V	Ti	Fe
7.9	Ø	¶	37	750	Ø	¶	37	1300
15	Ø	¶	+	Ø	43	¶	+	Ø
30	36	¶	+	Ø	63	¶	+	Ø
60	Ø	+	+	Ø	Ø	+	+	Ø

304L CRES

Exposure Time, Days	316.5°K (110°F)				344.3°K (160°F)			
	Cr	Fe	Mn	Ni	Cr	Fe	Mn	Ni
7.9	275	975	26	Ø	320	2700	8	¶
15	Ø	Ø	Ø	Ø	Ø	Ø	10	Ø
30	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø
60	Ø	Ø	Ø	170	Ø	Ø	Ø	272

Note: All concentrations are in parts per billion by weight.

Legend:

- Ø Sample - Blank < 0
- ¶ Sample - Blank < Error
- +

this may be due to a lack of experience with monomethylhydrazine in AAS analysis. There is no evidence of metal buildup as a function of either time or temperature. The materials are apparently compatible over the range of test conditions. The skeletal amount of information permits no further conclusions to be drawn.



## 5.0 FEASIBILITY DEMONSTRATION OF THE USE OF ELECTRICAL IMPEDANCE MEASUREMENTS TO DETERMINE THE EFFECT OF HYDRAZINE ON ALUMINUM SURFACES

### 5.1 INTRODUCTION

Investigations on the reaction between aluminum and hydrazine have produced discordant results. However, at least under some conditions, hydrazine has caused corrosion of aluminum [4-2]. This corrosion is dependent on the aluminum alloy, the hydrazine purity and the temperature.

In normal environments aluminum is covered by a protective oxide layer. The solubility of this oxide in water is very low but is increased in acidic or alkaline solutions. The oxide is very hard to reduce. For example, the free energy change,  $\Delta F_{298}^{\circ}$ , for the reaction  $3N_2H_4 + 2Al_2O_3 = 3N_2 + 6H_2O + 4Al$ , is +321 Kcal [5-1]. With such a high positive free energy change, the reduction by hydrazine is not found.

The solubility of aluminum or aluminum oxide in hydrazine appears to be very slight. However, when hydrazine was stored in 2014 aluminum, a precipitate was observed containing aluminum and copper [5-2]. This dissolution and precipitation appears to be similar to corrosive reactions in water where there is local solubility followed by precipitation of the dissolved product.

Impedance measurements have been used to study changes in the thickness due to the dissolution of the surface oxide on aluminum by various aqueous solutions [5-3]. By this means the initial step in the corrosion reaction is observed. Thus an effect on the aluminum (oxide) surface can be observed long before visible corrosion can be noticed.

Impedance of surface oxide layers on metals are generally determined by making the metal one plate of a capacitor and a platinum electrode in an aqueous salt solution the other plate. Concentrated salt solutions are used to keep the resistance of the solution low to avoid loss in accuracy in determining the oxide impedance. The impedance has also been

determined by forming the second plate of the capacitor by evaporating metal on top of the oxide [5-4].

It is not possible to determine the impedance of the oxide in hydrazine using the liquid as a conducting medium since its resistance is too high [5-5]. One might consider evaporating a metal layer on top of the oxide. However, it would tend to protect the oxide or otherwise effect the course of a corrosive reaction. For these reasons it has been decided to measure the impedance of the oxide layer in aqueous solution before and after exposure to hydrazine. Since aluminum will quickly oxidize in air and water a decrease in oxide thickness can be observed only if the oxide is first thickened anodically beyond its equilibrium thickness in contact with the aqueous solution. The effect of the hydrazine on the surface oxide can then be determined from the difference in the "before" and "after" impedance measurements.

## 5.2 THEORETICAL BACKGROUND

The electrical impedance of an oxide layer has a capacitive and a resistive or dissipative component. The thickness of the layer is obtained from the capacitive component. The thickness,  $d$ , is given by,

$$d = \frac{A Kr}{C 4 \pi} \quad (5.1)$$

where:  $A$  is the area of the capacitor,  
 $K$  is the dielectric constant,  
 $r$  is the roughness factor,  
and  $C$  is the capacitance.

The dielectric constant of thin surface oxides on aluminum is larger than that of thick anodic layers where the value is about 9 [5-6]. The dielectric constant increases as the dissipation, or loss tangent, increases.

The relation between dielectric constant and loss tangent has been given as [5-7].

$$K = 9 \left( \frac{10^7}{\nu} \right)^{\frac{2}{\pi} \tan \delta} \quad (5.2)$$

where  $\nu$  is the measuring frequency and  $\tan \delta$  is the loss tangent or dissipation.

For typical loss angles,  $\delta$ , of about  $4^\circ$ , the dielectric constant increases about 10% for a one degree increase in the loss angle. Thus, when we wish to find possible changes in oxide thickness due to hydrazine exposure we must take into account possible changes in loss angle as well as in capacitance.

Although the roughness factor,  $r$ , is greater than one and depends on the pre-treatment of the surface and on the particular alloy used, it would not be expected to change due to hydrazine exposure before gross corrosion began.

In actual measurements using a platinum counter electrode and a conducting salt solution, the impedance includes that of the salt solution and any layers on the platinum. Experimentally, the impedance of the platinum surface can be neglected and the salt solution can be treated as a pure resistance. Therefore, the equivalent series capacitance,  $C_s$ , obtained from the magnitude of the impedance,  $Z$ , and the phase angle,  $\theta$ , ( $\theta = 90 - \delta$ ) by the relation,

$$1/C_s = 2 \pi \nu Z \sin \theta, \quad (5.3)$$

is the capacitance of the surface oxide alone.

At low frequencies the impedance of the oxide on aluminum becomes much larger than that of the solution so that the measured phase angle below about 100 hertz for typical layers is due to the dissipation of the oxide layer alone. In practice, most samples have a high enough phase angle,  $\theta$ ,

at 100 hertz so that  $\sin \theta \approx 1$  and the inverse capacitance is directly proportional to the impedance. For samples which have similar roughness factors and phase angles, the impedance,  $Z$ , at 100 Hz can be used to compare thicknesses.

The oxide layer cannot be treated as a simple homogeneous substance between parallel plates of a capacitor, however. There is always a thin "barrier layer" next to the metal. This is an impervious layer covering the metal to a thickness dependent on either the temperature of oxidation in air or to the effective anodization voltage in an aqueous solution. The increase in thickness of the barrier layer on anodization is about 13 angstroms per volt.

Above this layer is a more complex layer, porous, partially hydrated and partially crystalline. It may be much thicker than the barrier layer and is greatly variable depending on the history of the surface especially on any etching treatments. When samples are anodized in a solution such as neutral boric acid, the barrier layer thickens below the outer layer which remains in place.

The impedance of the barrier layer may be treated as a homogeneous medium between plates of a capacitor although its dissipation may vary across the thickness. The impedance of the outer layer is quite variable. When this layer is being formed during an aqueous solution treatment its impedance is quite low since the solution penetrates to the barrier layer. However, it may become less permeable due to hydration or due to reduction in the wettability of the internal surfaces. Thus a freshly prepared sample may have an impedance largely due to the barrier layer but this impedance often increases on standing due to the increase of the outer layer. Drying at room temperature or in an oven will give a higher impedance than that of a freshly etched or anodized sample.

### 5.3 EXPERIMENTAL DEMONSTRATION

The experimental program adopted was to measure the electrical impedance of the surface oxide on an aluminum sample in a salt solution,

then to immerse the sample in hydrazine for a given period, and then repeat the impedance measurement.

The cell used to measure impedance is shown in Figure 5-1. It consisted of a plastic container containing a platinum counter electrode. The sample was clamped onto an O-ring gasket over a hole in the container. This container was connected by tubing with another vessel which was used to fill the measuring container. A slight flow of solution occurs when samples are being changed, which serves to keep air bubbles from forming under the sample. The impedance of the platinum electrode was small enough so that it did not make up an appreciable part of the impedance of the cell. Periodic checks with a piece of platinized platinum in place of the sample were used to assure the constancy of the cell impedance.

The diameter of the circle of liquid in contact with the aluminum sample was 0.40 cm. A saturated sodium sulfate solution, (saturated with aluminum oxide), was used as the electrolyte liquid. This solution has a relatively low electrical resistance and does not react with the oxide covered aluminum if the oxide is above a minimum thickness.

The impedance between the aluminum and the platinum was determined with a Hewlett-Packard Vector Impedance Meter, Model 4800A. High accuracy was assured by recording the magnitude and the phase angle of the impedance on a strip chart recorder and by calibrating the impedance meter versus high quality capacitors and resistors. The impedance can be measured between 5 hertz and 500 kilohertz.

The samples consisted of 3/4" x 2" sheets of either 99.99% pure aluminum or 2219-T87 aluminum alloy.

Most samples were prepared by first dissolving the as-received oxide in a sodium hydroxide solution followed by a dip in nitric acid. A few samples were prepared by etching in a chromic acid or hydrofluoric-nitric acid solution. After etching the samples were anodized to a small voltage in a solution prepared by neutralizing with ammonium hydroxide.

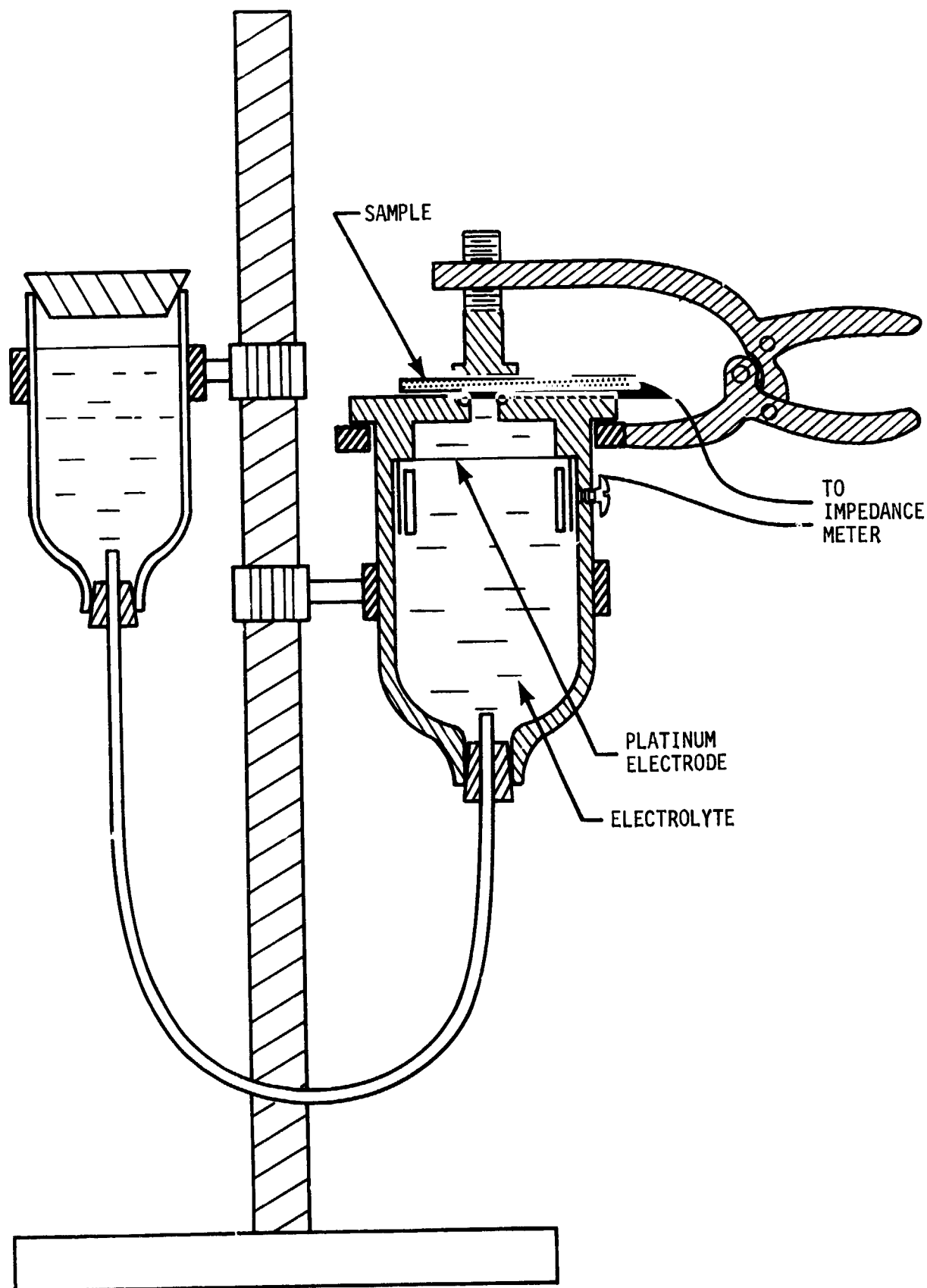


FIGURE 5-1: IMPEDANCE MEASURING CELL

This anodization produced a uniform oxide layer slightly thicker than the thinnest oxide stable in water. Thus, if hydrazine caused a thinning of this oxide it would be measurable; whereas a thinner film might reoxidize in the measuring solution and return to its original thickness. Most of the samples were dried in an oven to 130°C before impedance measurements were made.

The samples were bound with pure aluminum wire in bundles of three such that all the surfaces were exposed and then treated with military specification grade hydrazine in the cell shown in Figure 5-2. It was designed so that the samples may be placed in the cell and the volume flushed out with nitrogen through the Teflon valves followed by hydrazine being forced in under nitrogen pressure.

After removal from the hydrazine, the samples were rinsed quickly and thoroughly with cold water to avoid any reaction in the hydrazine-water mixture.

Impedance measurements were made on two areas of each sample before hydrazine treatment and two adjacent areas afterwards. It was not possible to place the O-ring hole on the identical spot a second time, so adjacent areas were used to avoid placing the hole over the mark left by the O-ring.

#### 5.4 EXPERIMENTAL RESULTS

The impedance measurements have been used to study changes in the thickness of the oxide layer of aluminum in the presence of military grade hydrazine. The impedance of such an oxide layer was largely capacitive.

For the geometry used here, the specific inverse capacitance,  $A/C_s$ , was, from Eq. 5.3,

$$A/C_s = 7.5 \times 10^{-5} \sqrt{Z \sin \theta}.$$

FIGURE 5-2: HYDRAZINE EXPOSURE CELL



where,  $\nu$  is the frequency in Hz  
 $Z$  is the magnitude of the impedance in ohms  
 $\theta$  is the phase angle in degrees  
and  $A/C_s$  is given in angstroms.

At 100 hertz where the phase angle,  $\theta$ , is close to  $90^\circ$ , the capacitance was

$$A/C_s = 7.5 Z_{100} \left( \frac{\text{angstroms}}{\text{kilo ohms}} \right)$$

When  $\frac{Kr}{4\pi} \approx 1$  one gets from Eq. 5.1,

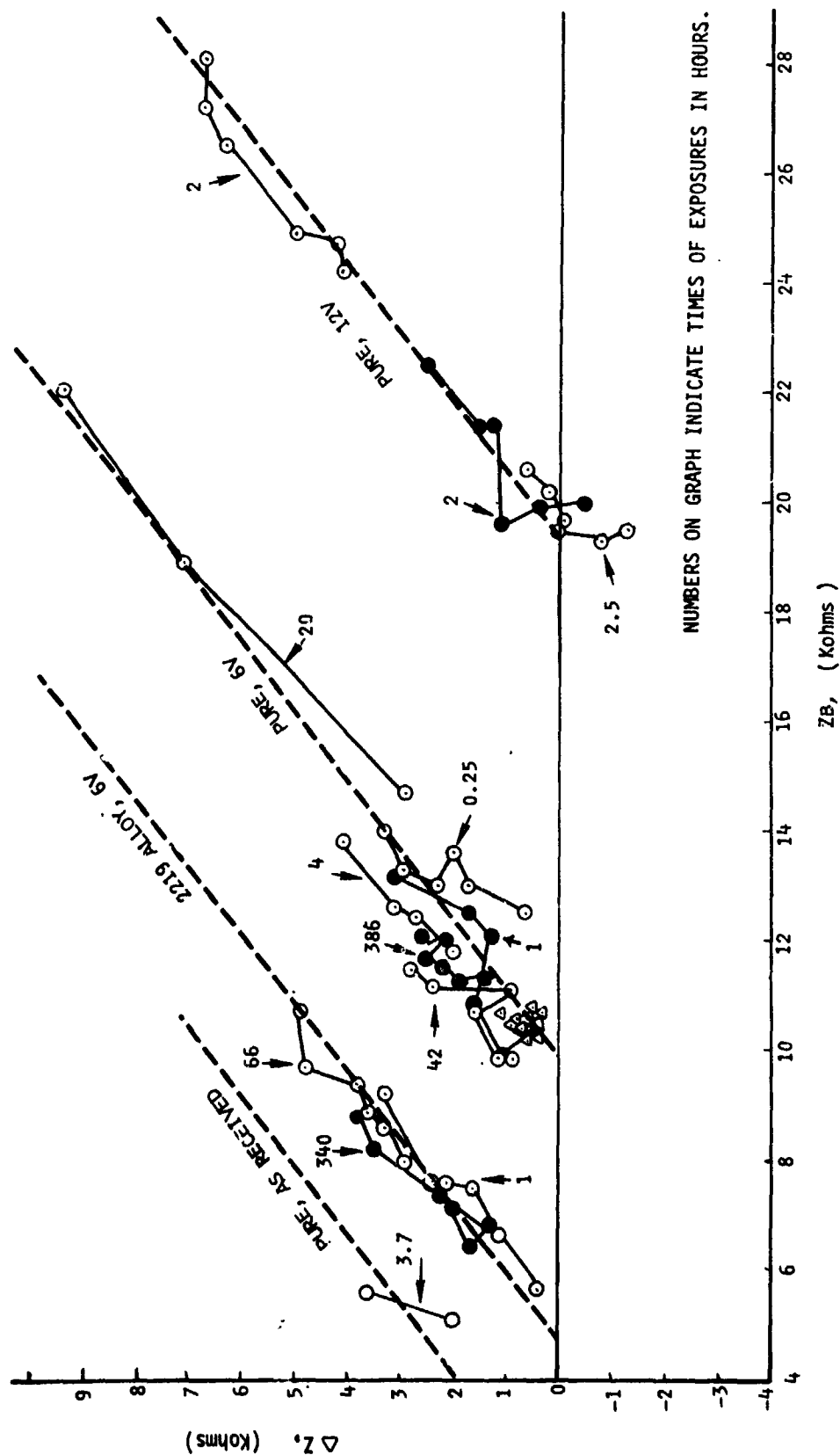
$$d \approx 7.5 Z \left( \frac{\text{angstroms}}{\text{kilo ohms}} \right).$$

Exposure of aluminum to hydrazine almost always results in a decrease in the electrical impedance of the surface oxide corresponding to a decrease in oxide thickness. Figure 5-3 shows the more significant aspects of these experiments. For a given alloy and a given anodization voltage, the decrease in impedance,  $\Delta Z$ , at 100 hertz increases with the initial impedance,  $Z_B$ .

If there were only a barrier layer oxide all of the impedance values,  $Z_B$ , for a given alloy and anodization voltage should have the same value except for minor variations in the roughness factor. The fact that there was a large spread of  $Z_B$  values indicates that there was a significant thickness of the outer layer in addition to the barrier layer. Note that, for samples which were not dried in the oven before determining  $Z_B$ , there is only a small spread in  $Z_B$  and a small  $\Delta Z$ .

The solid lines in Figure 5-3 connect samples prepared and treated at the same time. The dotted lines give the trend for samples of the same alloy and anodizing voltage. The meaning given is that the value of the impedance of the outer layer is that amount beyond the intersection of the dotted line with the abscissa. The barrier layer impedance is that value

△, NON-DRIED SAMPLES



NUMBERS ON GRAPH INDICATE TIMES OF EXPOSURE IN HOURS.

FIGURE 5-3: DECREASE IN IMPEDANCE,  $\Delta Z$ , DUE TO HYDRAZINE EXPOSURE VERSUS INITIAL IMPEDANCE,  $Z_B$

given by this intersection. Thus the intersection for the 12 volt samples is about twice that for the 6 volt samples. Therefore, the hydrazine reduces the impedance of the outer layer. The dotted lines are drawn for a decrease due to the hydrazine treatment of the impedance of the outer layer by 80%.

The major conclusion drawn from the results presented in Figure 5-3 was that hydrazine penetrated the outer oxide layer and modified it so that its impedance was greatly reduced. That the outer layer was not dissolved was shown by redrying a sample in the oven after the hydrazine exposure. The impedance after anodization was 11.2K ohms; after drying this increased to 16.0K ohms; a subsequent two-hour treatment in hydrazine reduced this to 11.8K ohms; and after redrying it went back up to 16.0K ohms. Thus, the outer layer was not dissolved nor was it modified irreversibly.

There was no indication of appreciable penetration of the barrier layer by hydrazine. One way to further explore this is by reanodization. When a sample is reanodized in a barrier layer forming electrolyte, there will be little current flowing as the voltage is increased until it reaches a value where the barrier layer thickness starts to increase. Thus, if there was any thinning or penetration of the barrier layer, the reanodization current will increase at a voltage lower than if there were no thinning. Figure 5-4 shows the results of such an experiment. After an initial anodization to 6 volts, a reanodization caused little current to flow until 6 volts was again approached. When a sample which had been exposed to hydrazine for 386 hours was reanodized, the result was much the same although the current was slightly higher. This result indicated that the barrier layer was essentially intact after the hydrazine treatment.

The fact that the 2219 alloy had an impedance about half of that of similar 6 volt anodized pure aluminum can be explained by a roughness factor about twice that of pure aluminum. (The alloy samples were machined which gives a high surface roughness and the etching of alloys tends to roughen them more than it does pure aluminum.) Otherwise, the results were similar for the alloys and for the pure aluminum.

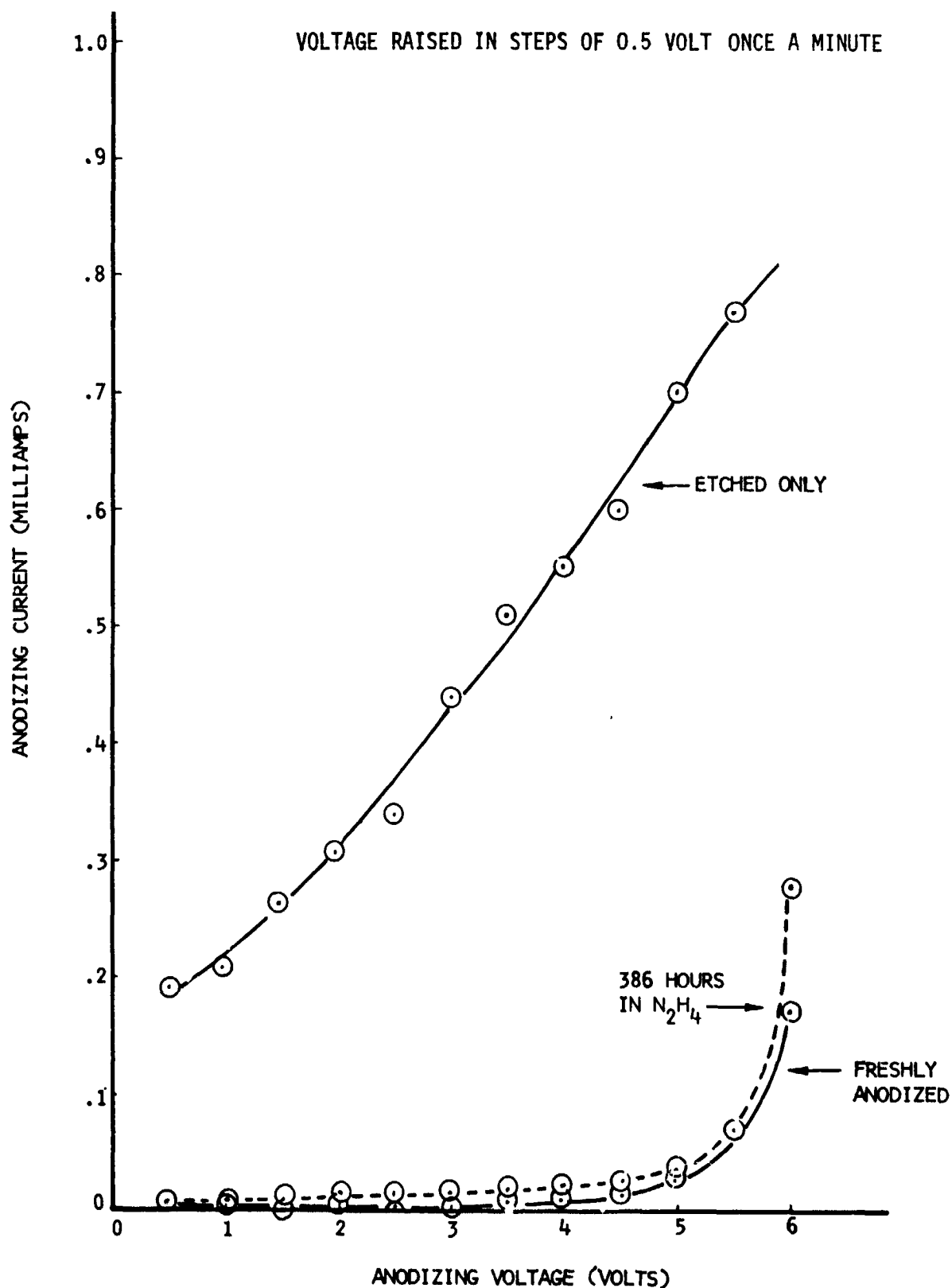


FIGURE 5-4: ANODIZING CURRENT VERSUS ANODIZING VOLTAGE.

There was either a small or zero time dependence of the hydrazine exposure. The pure sample was exposed between 0.25 and 386 hours. As seen in Figure 5-3, there was a slight tendency for the  $\Delta Z$  of the shortest exposures to be less than those of the higher exposures. However, the scatter of the data was such that no definite effect can be postulated. There was no appreciable time effect for the alloy samples exposed between one to 339 hours. These results indicated that the outer layer of oxide was penetrated rapidly and that no appreciable effect took place thereafter.

## 5.5 CONCLUSIONS

This work showed that the impedance technique is a valid method for observing changes on the oxide covered surface due to hydrazine exposure. These results indicated that hydrazine penetrates and interacts with the outer layer of the oxide but that the hydrazine did not dissolve the outer layer nor did it appreciably penetrate the barrier layer.

Since corrosive attack requires at least a thinning of the barrier layer it may be concluded that at room temperature there was no evidence of corrosive attack on either 99.99% pure aluminum or 2219-T87 aluminum alloy after over two weeks exposure to hydrazine. This is in concert with the work of Salvinski [4-28].

Under conditions of longer exposures, elevated temperatures, presence of impurities and different metals in contact, corrosion may occur. The impedance technique is capable of showing the initial stages of corrosive attack involving the thinning of the barrier layer. To achieve the most sensitivity it would be desirable to minimize the effect of the outer layer. This would be possible by briefly treating the sample with hydrazine before the first impedance measurement and then exposing the sample under the desired conditions.

## 6.0 HYDRAZINE MONOLAYER BUILDUP TESTING

### 6.1 BACKGROUND

Previous studies of flow decay problems by Pullen [6-1] have shown that radiotracers used to detect changes in the behavior of a hydrazine flow system, tend to deposit on fine screen-type filters along with metal contaminants contained in the hydrazine. Relatively small amounts of the radiotracers were found to be deposited in these experiments, being less than 1% of the total available tracer. However, limited flow time was accumulated (10 minutes per test) and there were uncertainties in the ultimate material deposition that would occur. Consequently, experiments were designed to study this deposition of metal contaminants in a hydrazine flow system during long flow times.

### 6.2 EXPERIMENTAL PROGRAM

The apparatus shown in Figures 6-1 and 6-2 was used in this study. The supply and catch tanks were constructed of type 2014 aluminum and the connecting tubing (1/4 inch O.D.) was of type 5052 aluminum. Flow rates were determined by measuring the pressure drop across the previously calibrated 0.0788 inch diameter orifice. The  $N_2H_4$  passed through a plate containing four 0.021 inch diameter orifices which limited the flow rate to the range previously studied (0.2 gal./min. to 0.38 gal./min.) [6-1].

Approximately two gallons of specification grade  $N_2H_4$  (MIL-P-26536C) was transferred to the supply tank and the radioactive tracer added. The as-received  $N_2H_4$  showed a metals content of 0.6 ppm iron and no zinc ( $<0.1$  ppm). The solution was repetitively cycled through a 10 micron absolute screen type filter (Western Filter Co. part number S12-19310-2) and the radioactivity buildup on the filter monitored by use of the sodium iodide scintillation detector and the attendant counting equipment discussed in Section 4. The supply tank pressure was set at 40 psig which resulted in a flow rate of 0.25 gal./min. The hydrazine was flowed at ambient temperature (55-60°F).

RECEDING PAGE BLANK NOT FILMED

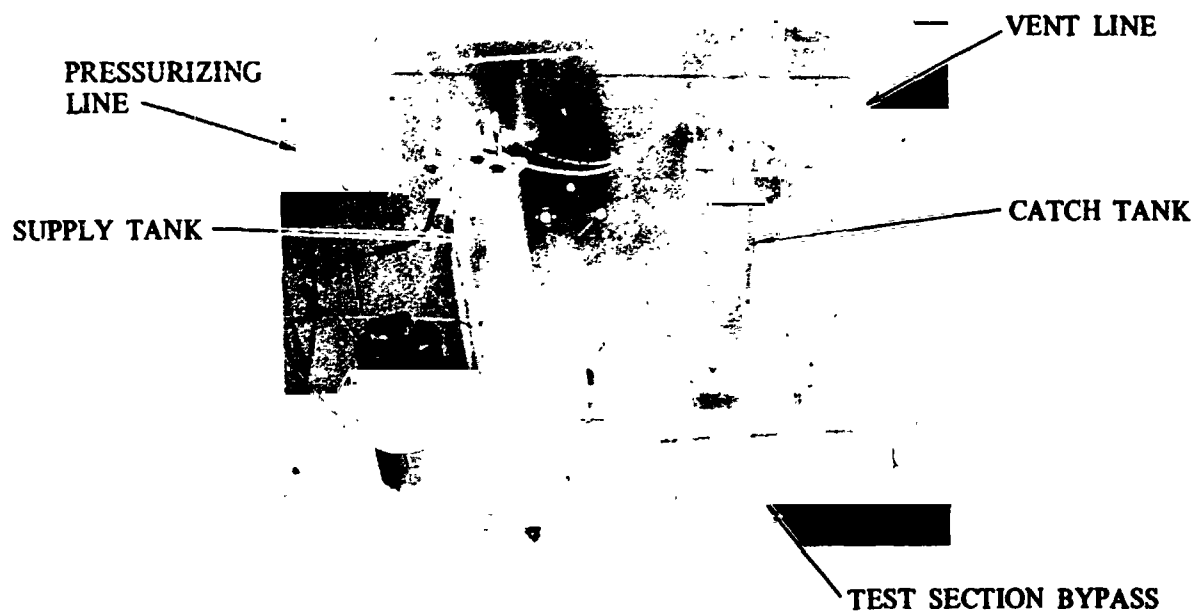


FIGURE 6-1: STANDARD FLOW SYSTEM HARDWARE

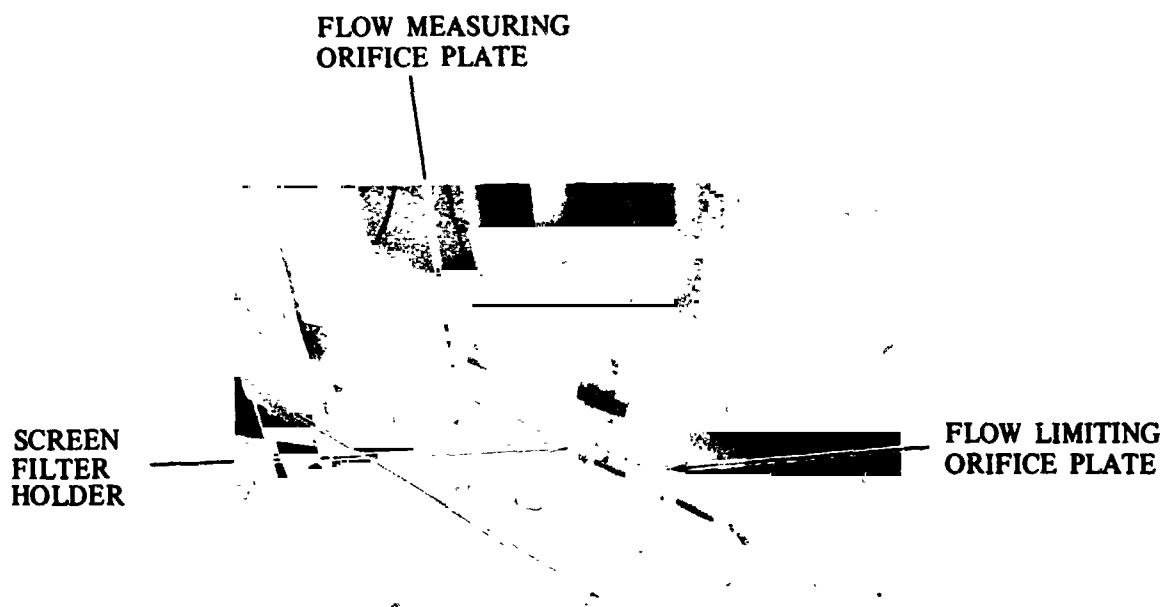


FIGURE 6-2: CLOSE-UP OF SCREEN FILTER AREA

### 6.3 EXPERIMENTAL RESULTS AND DISCUSSION

Tables 6-1 through 6-4 and Figures 6-3 through 6-6 summarize the radioactive buildup data for specification grade  $N_2H_4$  and, for comparison, deionized water where iron-59 was used as a tracer. Flow tests were conducted with deionized water (Table 6-1, Figure 6-3) to determine whether the radioactive buildup was common to other liquids. It was not. The  $H_2O$  flow tests were conducted under conditions identical to the  $N_2H_4$  tests (same  $Fe^{59}$  content, same flow rate, etc.), but the amount of deposition was much less. With  $H_2O$ , about 400 counts per minute (CPM) above background were found, corresponding to only a 0.25% deposition. After seven runs, 100 ml of concentrated nitric acid was added (giving a pH of 0.8), and the count rate decreased to 150 CPM (0.09% deposition).

By contrast, the  $Fe^{59}$  buildup in the  $N_2H_4$  tests was steady for about an hour (Table 6-2, Figure 6-4). Towards the end of that time the rate of buildup showed signs of declining somewhat. The system had to then be shut down at the end of the day. Upon resuming flow the next day, the count rate was initially depressed. However, after about one hour of flow the count rate regained its former value and remained essentially constant, corresponding to a 1.42% deposition of the  $Fe^{59}$  tracer added to the  $N_2H_4$ . (Interrupting the flow, venting and retransferring the  $N_2H_4$  from the catch tank to the supply tank characteristically caused small decreases in deposited radioactivity, which recovered during the subsequent run or runs.)

The small (1.42%) deposition raised the question as to whether a larger iron content in the  $N_2H_4$  would have resulted in a higher degree of deposition. To answer this question, 1.9 ppm of iron as ferric nitrate was added to another tankful of  $N_2H_4$  containing the same amount of tracers as before and the flow testing was repeated. As indicated in Table 6-3 and Figure 6-5, a gradual buildup again occurred but the final level of activity was much lower (0.33%). A comparison of Tables 6-2 and 6-3 shows that the percent iron deposited was very nearly inversely proportional to the total iron in the  $N_2H_4$ . In other words the total mass of iron (about 60 micrograms) that deposited was a constant. These results are consistent



with a mechanism in which the extent of deposition is limited by the number of available active sites on the surface of the filter. Surface adsorption and chemical interaction with the oxide layer of the stainless steel filter are two possible explanations.

Interatomic exchange between the radioactive  $\text{Fe}^{59}$  atoms of the added tracer and the iron atoms of the filter was considered to be a less likely explanation because of the lower deposition rate in the deionized water test. To further elucidate this question, radioactive zinc-65 was added to a fresh tank of hydrazine and a series of flow tests were run. Since there was no zinc in the stainless steel filter, interatomic exchange (and radioactive buildup) should not occur. However, radioactive buildup did occur in much the same manner as with iron-59. About 1.2% of the  $\text{Zn}^{65}$  radioactivity contained in the tank of  $\text{N}_2\text{H}_4$  was deposited on the filter. Also, the chemical entity responsible for the activity was quite adherent since the deposit could not be washed from the filter by back-flushing. See Table 6-4 and Figure 6-6.

Review of the experiments showed that only small amounts of materials accumulated on the filters. Buildup reached its equilibrium value after a total flow time of approximately an hour, and at least in the case of zinc, the deposit was adherent. No deposit could be detected during visual examination of the filters following flow testing and no flow decay was observed in any of the hydrazine tests. While the exact mechanism could not be ascertained without additional data, a surface effect such as adsorption of metal-hydrazine complexes by active sites on the filter appeared plausible. The fact that the amount of the metal deposit was independent of the metal concentration in the hydrazine suggests saturation of surface deposition sites. On the basis of these data, clogging of similar filters in operational use will not occur. This confidence should probably not be extended to filters with significantly smaller pore size.

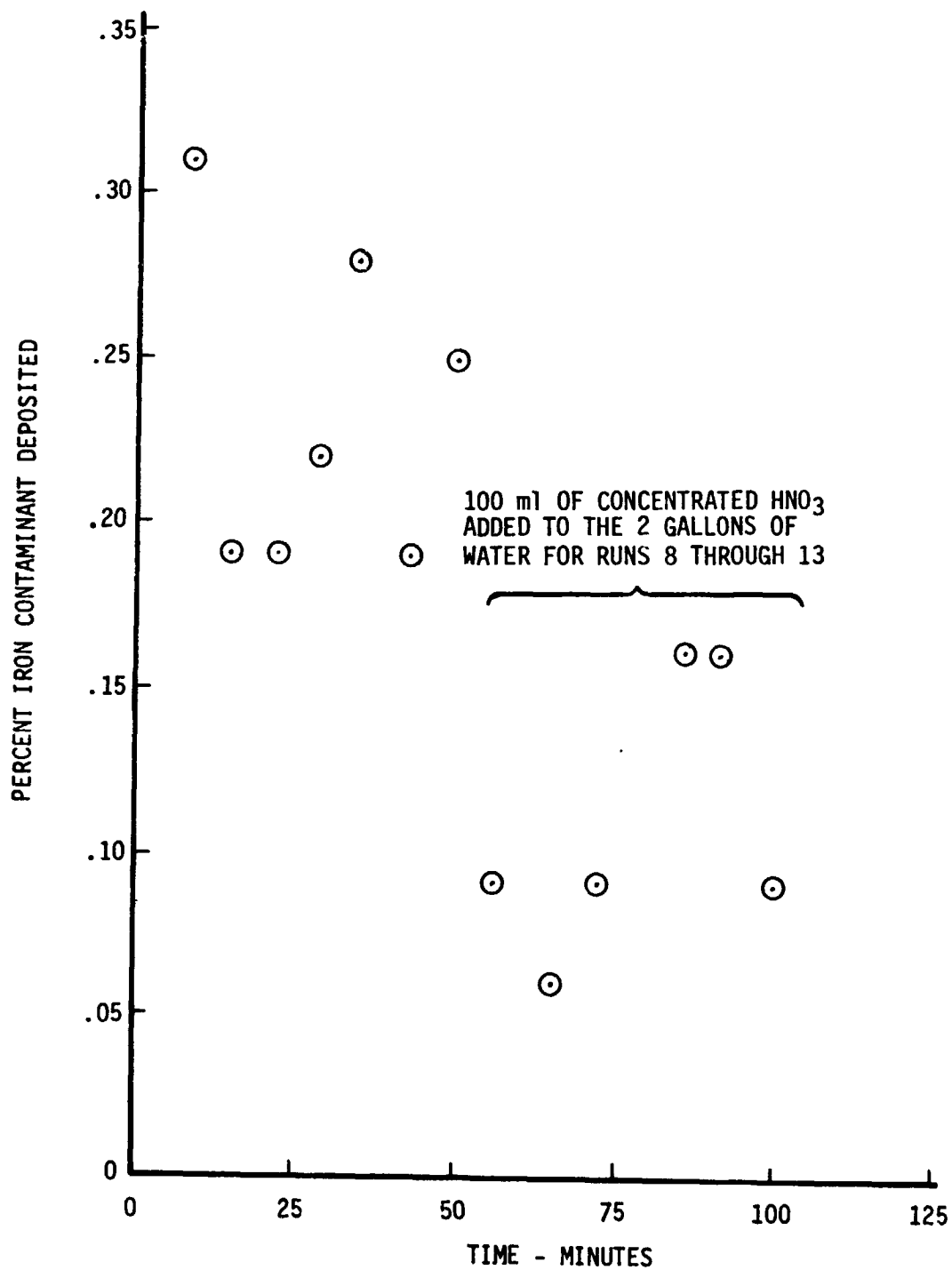


Figure 6-3: FLOW TEST INVOLVING WATER WITH IRON - 59 TRACER ADDED

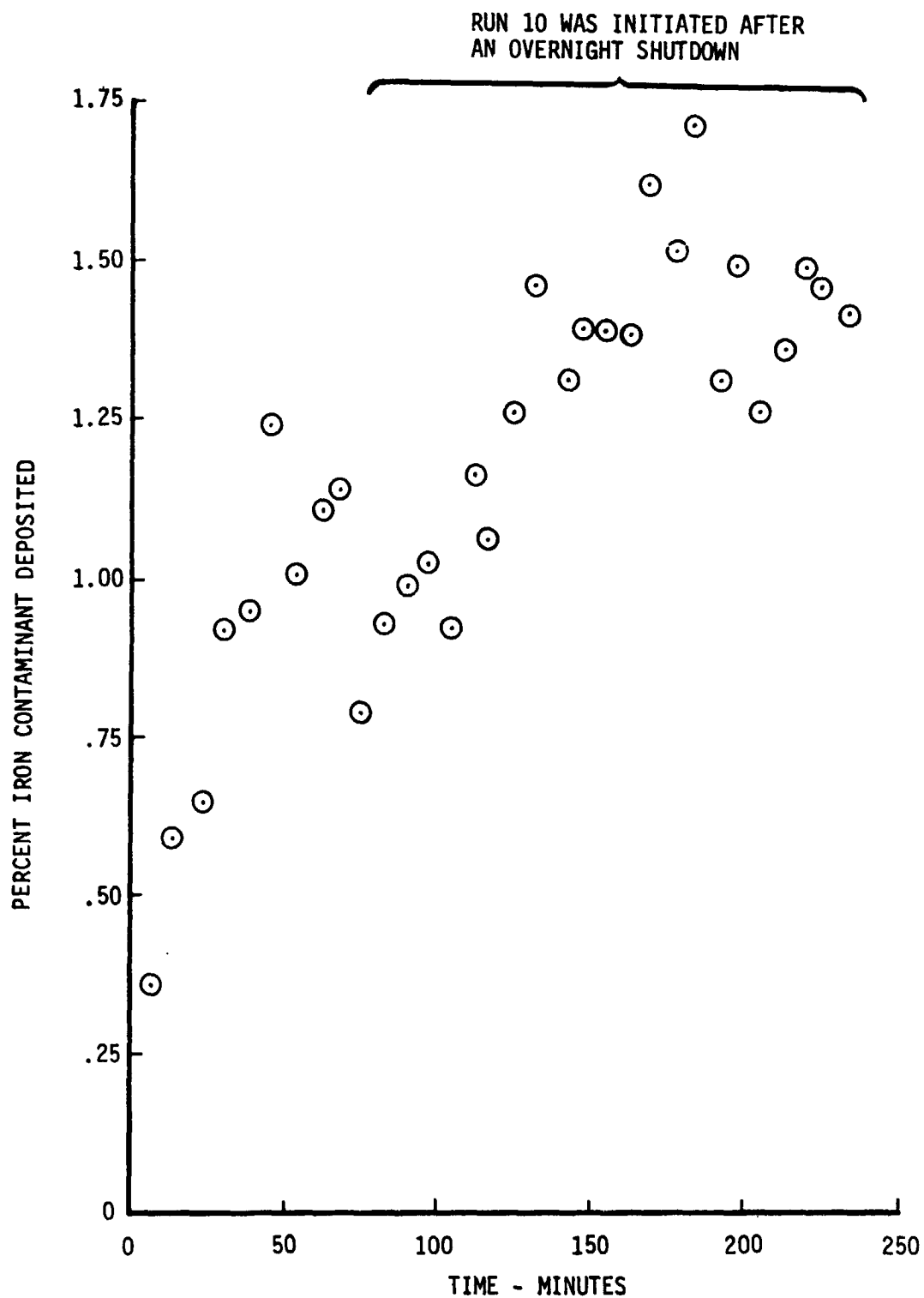


Figure 6-4: FLOW TEST INVOLVING HYDRAZINE WITH IRON - 59 TRACER ADDED

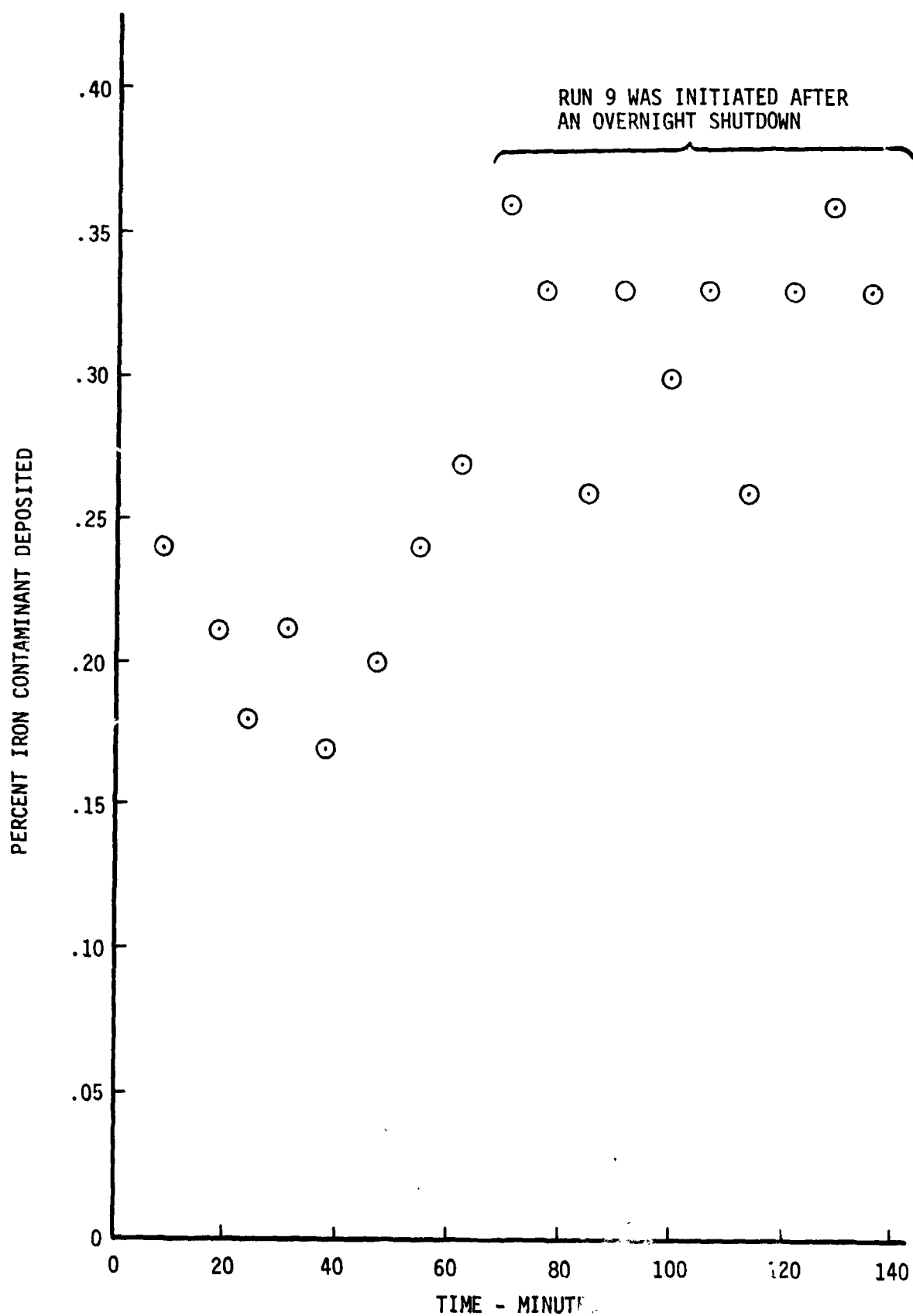


Figure 6-5: FLOW TEST INVOLVING HYDRAZINE WITH .9 PARTS PER MILLION DISSOLVED IRON ADDED IN ADDITION TO IRON - 50 TRACES

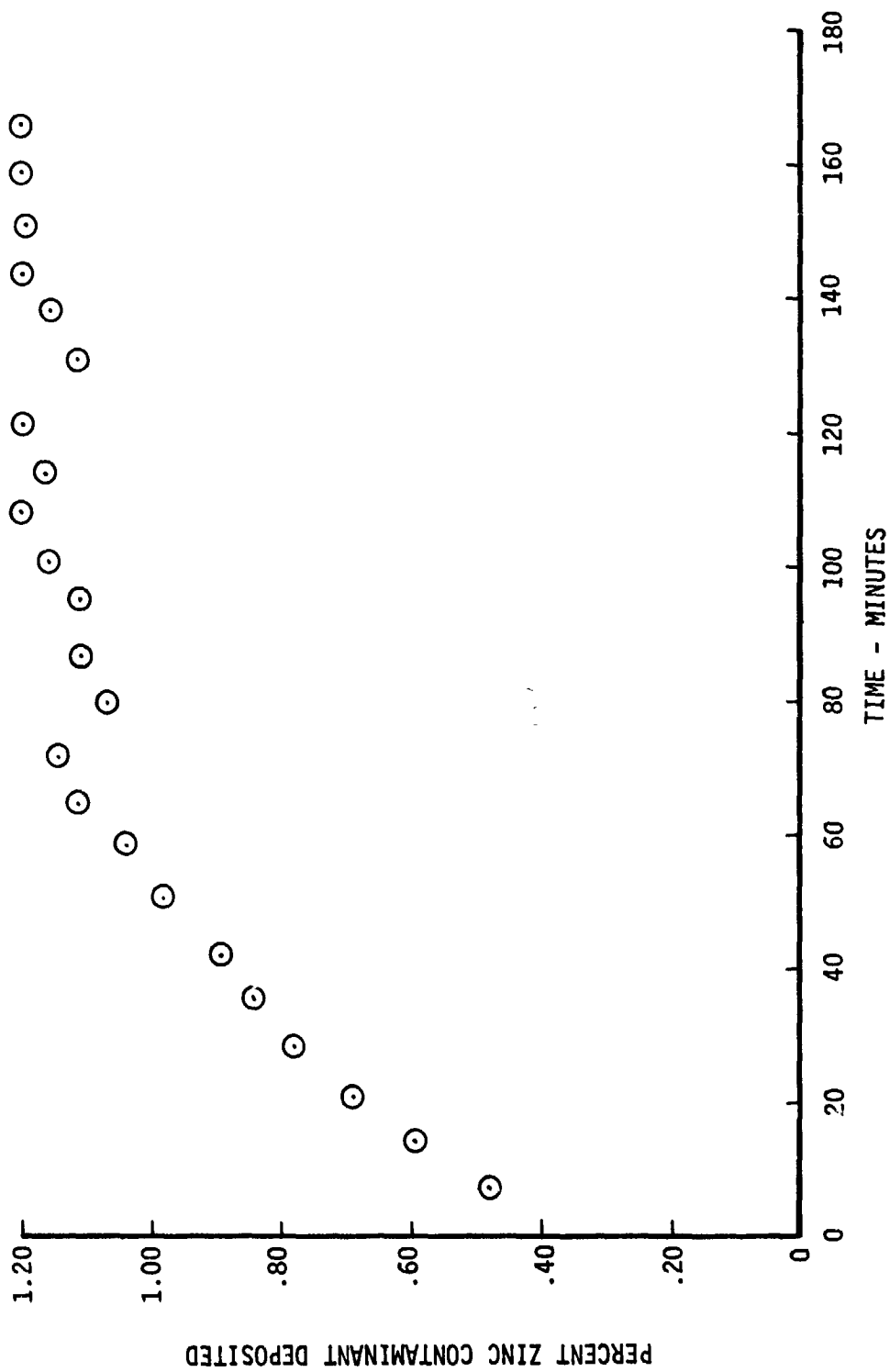


Figure 6-6: FLOW TEST INVOLVING HYDRAZINE WITH ZINC - 65 TRACER ADDED

RUN	CUMULATIVE FLOW TIME (MINUTES)	COUNTABLE RADIOACTIVITY ADDED TO H <sub>2</sub> O (CPM)	CUMULATIVE RADIOACTIVITY DEPOSITED ON FILTER (CPM)	CUMULATIVE IRON CONTAMINANT DEPOSITED (%)	TOTAL IRON PRESENT IN H <sub>2</sub> O (PPM)
1	8	1.62 X 10 <sup>5</sup>	500	0.31	< 0.05
2	15	"	300	0.19	"
3	22	"	300	0.19	"
4	29	"	350	0.22	"
5	35	"	450	0.28	"
6	43	"	300	0.19	"
7	50	"	400	0.25	"
-----					
8*	57	"	150*	0.093	"
9	66	1.60 X 10 <sup>5</sup>	100	0.063	"
10	73	"	150	0.094	"
11	81	"	250	0.16	"
12	91	"	250	0.16	"
13	100	"	150	0.094	"

\* 100 ml of CONC. HNO<sub>3</sub> ADDED TO THE 2 GALLONS OF WATER FOR RUNS 8 THROUGH 13

TABLE 6-1 FLOW TEST INVOLVING WATER WITH IRON-59 TRACER ADDED

RUN	CUMULATIVE FLOW TIME (MINUTES)	COUNTABLE RADIOACTIVITY ADDED TO N <sub>2</sub> H <sub>4</sub> (CPM)	CUMULATIVE RADIOACTIVITY DEPOSITED ON FILTER (CPM)	CUMULATIVE IRON CONTAMINANT DEPOSITED (%)	TOTAL IRON PRESENT IN N <sub>2</sub> H <sub>4</sub> (PPM)
1	8	1.53 X 10 <sup>5</sup>	550	0.36	0.6
2	15	"	900	0.59	"
3	23	"	1000	0.65	"
4	30	"	1400	0.92	"
5	38	"	1450	0.95	"
6	45	"	1900	1.24	"
7	53	"	1550	1.01	"
8	61	"	1700	1.11	"
9	68	"	1750	1.14	"
-----*					
10	75	1.51 X 10 <sup>5</sup>	1200*	0.79	"
11	83	"	1400	0.93	"
12	90	"	1500	0.99	"
13	97	"	1550	1.03	"
14	105	"	1400	0.93	"
15	112	"	1750	1.16	"
16	118	"	1600	1.06	"
17	125	"	1900	1.26	"
18	133	"	2200	1.46	"
19	141	"	2000	1.32	"
20	148	"	2100	1.39	"
21	155	"	2100	1.39	"
22	162	"	2100	1.39	"

\* Run 10 was initiated after an overnight shutdown.

TABLE 6-2 FLOW TEST INVOLVING HYDRAZINE WITH IRON-59 TRACER ADDED

RUN	CUMULATIVE FLOW TIME (MINUTES)	COUNTABLE RADIOACTIVITY ADDED TO N <sub>2</sub> H <sub>4</sub> (CPM)	CUMULATIVE RADIOACTIVITY DEPOSITED ON FILTER (CPM)	CUMULATIVE IRON CONTAMINANT DEPOSITED (%)	TOTAL IRON PRESENT IN N <sub>2</sub> H <sub>4</sub> (PPM)
23	169	1.51 X 10 <sup>5</sup>	2450	1.62	0.6
24	177	"	2300	1.52	"
25	184	"	2600	1.72	"
26	191	"	2000	1.32	"
27	198	"	2250	1.49	"
28	205	"	1900	1.26	"
29	212	"	2050	1.36	"
30	220	"	2250	1.49	"
31	227	"	2200	1.46	"
32	234	"	2150	1.42	"

TABLE 6-2 FLOW TEST INVOLVING HYDRAZINE WITH IRON-59 TRACER ADDED



RUN	CUMULATIVE FLOW TIME (MINUTES)	COUNTABLE RADIOACTIVITY ADDED TO N <sub>2</sub> H <sub>4</sub> (CPM)	CUMULATIVE RADIOACTIVITY DEPOSITED ON FILTER (CPM)	CUMULATIVE IRON CONTAMINANT DEPOSITED (%)	TOTAL IRON PRESENT IN N <sub>2</sub> H <sub>4</sub> (PPM)
1	9	1.04 X 10 <sup>5</sup>	250	0.24	2.5
2	17	"	220	0.21	"
3	24	"	190	0.18	"
4	31	"	220	0.21	"
5	39	"	180	0.17	"
6	47	"	210	0.20	"
7	55	"	250	0.24	"
8	63	"	280	0.27	"
-----					
9	71	1.03 X 10 <sup>5</sup>	370*	0.36	"
10	78	"	340	0.33	"
11	85	"	270	0.26	"
12	92	"	340	0.33	"
13	100	"	310	0.30	"
14	107	"	340	0.33	"
14	114	"	270	0.26	"
16	122	"	340	0.33	"
17	129	"	370	0.36	"
18	136	"	340	0.33	"

\* Run 9 was initiated after an overnight shutdown

TABLE 6-3 FLOW TEST INVOLVING HYDRAZINE WITH 1.9 PARTS PER MILLION DISSOLVED IRON ADDED IN ADDITION TO IRON -59 TRACER

RUN	CUMULATIVE FLOW TIME (MINUTES)	COUNTABLE RADIOACTIVITY ADDED TO N <sub>2</sub> H <sub>4</sub> (CPM)		CUMULATIVE RADIOACTIVITY DEPOSITED ON FILTER (CPM)	CUMULATIVE ZINC CONTAMINANT DEPOSITED (%)	TOTAL ZINC PRESENT IN N <sub>2</sub> H <sub>4</sub> (PPM)
		7	6.65 X 10 <sup>5</sup>			
1	7			3250	0.49	< 0.1
2	14		"	3900	0.59	"
3	21		"	4600	0.69	"
4	29		"	5200	0.78	"
5	36		"	5650	0.85	"
6	43		"	6000	0.90	"
7	51		"	6500	0.98	"
8	58		"	6900	1.04	"
9	66		"	7450	1.12	"
10	73		"	7600	1.14	"
11	80		"	7100	1.07	"
12	87		"	7400	1.11	"
13	95		"	7400	1.11	"
14	102		"	7700	1.16	"
15	109		"	8000	1.20	"
16	116		"	7700	1.16	"
17	123		"	8000	1.20	"
18	131		"	7400	1.11	"
19	138		"	7700	1.16	"
20	145		"	8000	1.20	"
21	152		"	7900	1.19	"
22	159		"	8000	1.20	"
23	166		"	8000	1.20	"

TABLE 6-4 FLOW TEST INVOLVING HYDRAZINE WITH ZINC-65 TRACER ADDED

## 7.0 CONCLUSIONS

Two important conclusions of a general nature are readily apparent. First, the objective of the program, the advancement of the state of the technology for determining the long term compatibility of materials with propellants, was achieved. This was accomplished by the development of a prediction method, the basis of which was the utilization of sensitive measurement techniques to derive basic kinetic rate expressions, that could be used to establish long-term compatibility information from short-term experimental data. Second, the partial application of the prediction method to the systems 6Al-4V titanium/hydrazine, 304L CRES/hydrazine, 6Al-4V titanium/fluorine, 6Al-4V titanium/FLOX, and 2219 aluminum/fluorine led to the conclusion that any corrosion-induced metal build-up in the propellant is small for long-term storage periods provided that the concentrations of  $\text{CO}_2$  in the 304L CRES/hydrazine system and HF in the 6Al-4V titanium/fluorine and FLOX systems are kept at sufficiently low levels.

The prediction method established in this program is based on an empirical part (the generation of compatibility data) and a theoretical part (the formulation of the kinetic rate expression). As such, it is an inclusive method that is applicable to any system. It is a vast improvement over previous approaches, such as simple extrapolation, which had no theoretical basis for the conclusions drawn and accelerated aging, which often yielded misleading results. The time required for the generation and reduction of data should ordinarily be only a few weeks, or months, and in that respect, it is a vast improvement over real-time testing.

An ideal prediction method might consist of a computerized "black box" into which one could physically place any material/propellant combination of interest, and after waiting a short time, the device would provide the necessary long-term compatibility information. Such an ideal device, while highly desirable, cannot readily be constructed because of the magnitude and complexity surrounding the question of compatibility.

PRECEDING PAGE BLANK NOT FILMED

The method described in this program is applicable to any system, but the exact empirical set-up may vary widely because of the different experimental constraints that may have to be placed on any particular material/propellant pair.

Focusing on the data generated in this program, several useful conclusions relating to long term compatibility can be drawn, even though further data are needed to refine the kinetic expressions postulated. The alloy 6Al-4V titanium showed no interaction at all (as measured by metal buildup in the propellant) in hydrazine containing up to 50 ppm chloride as NaCl. It was concluded that deleterious levels of metals would not be generated in  $N_2H_4$  containing up to 50 ppm chloride (as NaCl) for at least 10 years. It was further concluded that a distinction should be made between "active" chloride (Hydrazinium chloride, an acid in hydrazine) which allegedly attacks 6Al-4V titanium [4-23] and "inactive" chloride (such as the salt NaCl) which does not.

Carbon dioxide, which forms the acid hydrazinium carbazate in hydrazine, readily corroded the surface of the 304L CRES specimens. The metal buildup data were best explained by a two-part mechanism. The first was a comparatively slow zero-order reaction of 30 days duration (for  $S/V = 0.689 \text{ cm}^{-1}$ ) during which dissolution of the protective metal oxide occurred. The second part was a first-order reaction with respect to  $CO_2$  concentration having a rate constant of  $k = 0.0432/\text{day}$ . Both parts were concluded to be essentially independent of temperature in the range 110-160°F. The fact that the protective oxide coating postponed the onset of the first-order hydrazinium carbazate attack is an argument in favor of the passivation procedure used in this program that generated a protective oxide coating on the CRES surface. As in the case of chloride in the titanium/hydrazine system, a distinction should be made between "active"  $CO_2$  (hydrazinium carbazate, a corrosive acid in hydrazine) and "inactive"  $CO_2$  (such as a metal carbazate, which cannot react with a metal surface).

One of the most important conclusions reached in the 6Al-4V titanium/fluorine and FLOX tests was that the presence of HF could significantly affect the rate of corrosion as measured by metal buildup in the propellant. Although an exact kinetic rate expression was not

established, predictions were still made based on conclusions that the rate of buildup for a given HF concentration could occur no faster than an assumed zero-order rate expression. Using the maximum rates thus calculated, it was concluded that at low (0.008%) concentrations of HF, the amount of corrosion after several years contact time would be acceptably small.

The 2219 aluminum/fluorine system was different from the 6Al-4V titanium/fluorine system in that no HF dependence was found, but a temperature dependence was observed. Again an exact kinetic expression could not be derived, but the data closely approximated the dependence one could expect from zero-order kinetics, with a value of  $k = .85 e^{-316/RT}$  ppb Al/hr. Even at the higher values of the temperature, the amount of metal buildup was acceptably small after five years.

In summary, then, it was possible to develop a useful method for prediction of propellant-material compatibility. As an added bonus, some valuable engineering data on several candidate propellant-materials pairs were generated.

## 8.0 RECOMMENDATIONS

Three major areas of this program are prominently in need of further work. The first involves strengthening of the prediction method and increasing its utilization by application of computer methods. The second and third deal with broadening our fundamental knowledge of the role of impurities such as  $\text{N}_2\text{H}_5^+$ ,  $\text{CO}_2$  and  $\text{Cl}^-$  in hydrazine and HF in liquid fluorine. A fourth area, the comparison of long-term predictions with actual long term data, was not a part of the current program and awaits a future effort.

Computer programs dealing with long-term compatibility predictions are desirable because of the overall complexity of the subject matter. The general flow diagram shown in Figure 2-1 and the related subsidiary flow diagrams readily lend themselves to programming methods. Extensive data storage and retrieval could also be accomplished by utilization of computers. An engineer desiring information relative to the long-term compatibility of a particular system could input the name of the material, the propellant and other pertinent facts. The computer could then output the existing available data and indicate which part, if any, of the flow diagram of Figure 2-1 needs additional analysis or testing to obtain the required information.

The tests involving hydrazine with CRES yielded some valuable rate data, but also raised some questions which require resolution. The rate expression postulated in this document should be confirmed with data obtained by using the more efficient radioactive tracer method. The atomic absorption technique required many measurements on a large number of CRES/hydrazine specimens, and the constraints of the predetermined reaction conditions were not conducive to an unambiguous determination of the rate expression. The data obtained in the current program were valuable in that they defined those reaction conditions upon which the radioactive tracer method should be focused.

As indicated elsewhere in this document, the presence of chloride did not affect the rate of attack of hydrazine on 6Al-4V titanium. This is in contrast to the results reported by Tolberg, et. al., at SRI [4-23].

PRECEDING PAGE BLANK NOT FILMED

An explanation for the apparent difference in results is that in the present study chloride was added as NaCl, while in the SRI study it probably had been present as hydrazinium chloride ( $\text{N}_2\text{H}_5^+\text{Cl}^-$ ). The species responsible for the corrosion in the latter study most likely was the acidic (in  $\text{N}_2\text{H}_4$  solution)  $\text{N}_2\text{H}_5^+$  ion, the same ion formed when  $\text{CO}_2$  reacts with  $\text{N}_2\text{H}_4$  to form hydrazinium carbazate ( $\text{N}_2\text{H}_5^+\text{CO}_2\text{N}_2\text{H}_3^-$ ). Although the concentration of the  $\text{N}_2\text{H}_5^+$  cation may be of major importance, the role played by the anion involved cannot be ignored, since, in contrast to hydrazinium chloride, hydrazinium carbazate seems to be relatively unreactive toward 6Al-4V titanium [4-28]. Clearly, there is a need to quantify the rate of reaction of  $\text{N}_2\text{H}_4$  with various alloys in the presence of  $\text{N}_2\text{H}_5^+$ ,  $\text{CO}_2$ , and  $\text{Cl}^-$ . Also, work should be undertaken to establish a method for determining the amount of  $\text{N}_2\text{H}_5^+$  ion present in hydrazine, in order to set appropriate maximum limits in the specification. It is important that  $\text{Cl}^-$  and  $\text{CO}_2$  be determined by analytical methods that take into account whether these substances are "active" (that is, present as hydrazinium chloride and hydrazinium carbazate) or "inactive" (present as metal chlorides and metal carbazates).

The surface impedance measurement technique should definitely be applied to the hydrazine/CRES system. The data generated in this study suggested that  $\text{N}_2\text{H}_4$  contaminated with  $\text{CO}_2$  will slowly dissolve the protective stainless steel oxide layer and subsequently initiate a rapid attack on the unprotected metal surface. The surface impedance technique would be a powerful tool with which to confirm this proposed mechanism.

The tests involving 6Al-4V titanium with liquid fluorine and FLOX showed a rate dependence on the HF content of the oxidizer; these results should be investigated further. Although one might expect HF to be relatively unreactive at such low temperatures, there are very little data in the literature on the subject. Consequently, programs should be undertaken to derive basic information pertaining to the solubility of HF in liquid fluorine (and FLOX) and the reactivity of solutions or suspensions of HF in liquid fluorine (and FLOX).

Finally, all of the predictions utilizing short-term data made in this program should be compared to the fullest extent possible with long-term data generated elsewhere. Such data has been generated for both fluorine and FLOX by TRW [8-1] as well as hydrazine [4-13].



## 9.0 REFERENCES

- 1-1 Green, R. L., Advanced Techniques for Determining Long Term Capability of Materials With Propellants. Boeing Company Interim Report, D180-14839-1, Contract NAS7-789, June 1972.
- 2-1 Burdette, G. W. and Couch, D. H., Apparatus for Liquid Propellant Stability and Compatibility Studies. Naval Weapons Center Memo 4585-57-69, dated 3 April 1969.
- 2-2 "Recommended Practices for Static Immersion Testing of Materials in Liquid Propellants and Other Aerospace Fluids." JANNAF Liquid Propellant Test Methods, Test Number 726.0, Static Immersion, CPIA, March 1972.
- 3-1 Walsh, A., Spectrochim. Acta 7, 108, 1955.
- 3-2 Herzberg, G., Atomic Spectra and Atomic Structure. Dover Publications, Inc., New York, N. Y., 1944.
- 3-3 Anonymous, Technique and Applications of Atomic Absorption. Perkin-Elmer Corporation, Instrument Division, Norwalk, Connecticut, 1970.
- 3-4 Skoog, D. A. and D. M. West, Principles of Instrumental Analysis, Holt, Rinehart and Winston, Inc., New York, N. Y., 1971.
- 3-5 Massmann, H., Spectrochim. Acta, 23B, 215 (1968).
- 3-6 Kohn, H. L., Instrumentation for Atomic Absorption - Part One, J. Chem. Ed. 43, A7, (1966).
- 3-7 Anonymous, Analytical Methods for Atomic Absorption Spectroscopy Using the HGA Graphite Furnace, Perkin-Elmer Corporation Rpt. 990-9972, March 1973.
- 4-1 Salvinski, R. J., et al: Advanced Valve Technology, Volume II - Materials Compatibility and Liquid Propellant Study. TRW Systems Interim Report 06641-6014-R000, Contract NAS7-436, November 1967.
- 4-2 Uney, P. E. and Fester, D. A.: Material Compatibility With Space Storable Propellants Design Guidebook. Martin-Marietta Corp. Report MCR-72-26, Contract HF-5564.9 under NAS7-100, March 1972.
- 4-3 Vander Wall, E. M., et al: Dynamic Compatibility of Halogen Propellants. Aerojet Liquid Rocket Company, Report AFRPL-TR-72-118, January 1973.
- 4-4 Jackson, J. D., Compatibility of Materials With Fluorine and Fluorine-Base Oxidizers. Defense Metals Information Center, April 8, 1965.

- 4-5 Asunmaa, S. K., et al: Halogen Passivation Procedural Guide.  
McDonnell Douglas Final Report AFRPL-TR-67-309, December 1967.
- 4-6 Robertson, D. E., Role of Contamination in Trace Element Analysis  
of Sea Water. Analytical Chem., V40, N7, P1067, June, 1968.
- 4-7 Schmidt, H. W., Handling and Use of Fluorine and Fluorine-Oxygen  
Mixtures in Rocket Systems. NASA SP-3037, 1967.
- 4-8 White, E. L. And Ward, J. J., Ignition of Metals in Oxygen.  
DMIC Report 224, Defense Metals Information Center, Columbus,  
Ohio, February 1966.
- 4-9 Cannon, W. A., et al: Halogen Passivation Studies. AFRPL-TR-66-  
330, Astronpower Laboratory, Douglas Aircraft Company, January  
1967.
- 4-10 Kleinberg, S. and Thompkins, J. F., The Compatibility of Various  
Metals With Liquid Fluorine, Report No. ASD-TDR-62-250, Air  
Products and Chemicals, Inc., March 1962.
- 4-11 Lorentz, P. M., Compatibility of Tankage Materials With Liquid  
Propellants. AFML-TR-69-99, The Boeing Company, May 1969.
- 4-12 Fluorine Systems Handbook, NASA CR-72064, NASA Lewis Research  
Center, Contract NASw-1351, Douglas Aircraft Company, July 1, 1967.
- 4-13 Lona, H. R. and Bjorklund, R. A., Trajectory Correction Propulsion  
for TOPS, NASA TR-32-1571, Jet Propulsion Laboratory, November 15,  
1972.
- 4-14 Personal Communication with F. S. Forbes, Air Force Rocket  
Propulsion Laboratory, 1 June 1973.
- 4-15 Christopher, G. L. M. and Brown, C. T., Hydrazine Impurity Survey.  
AFRPL TR-73-24, United Aircraft Research Laboratories, June 1973.
- 4-16 Coulbert, C. D. and Yankura, G., Survey of Materials for Hydrazine  
Propulsion Systems in Multicycle Extended Life Applications.  
NASA TM 33-561, Jet Propulsion Laboratory, 15 September 1972.
- 4-17 Cadwallader, E. and Piper, Leland B., Hydrazine Compatibility  
Survey. CPIA Publication 236, June 1973.
- 4-18 Manning, D. C. and Fernandez, F., Atomization for Atomic Absorption  
Using a Heated Graphite Tube. Atomic Absorption Newsletter, Vol. 9,  
No. 3, May-June 1970.
- 4-19 Titanium Metals Corporation of America, "Certificate of Test,  
Notice of Shipment", Invoice Number 559-447, dated 3 January  
1967; forwarded to Boeing by L. R. Toth/JPL, 21 June 1973.

- 4-20 Cox, D. W., Specimen/Capsule Preparation Used on the JPL Material Compatibility Program. Pressure Systems, Inc., Rpt. 525902-1, April 1970.
- 4-21 Englehardt, P. M., General Specification, Long Term Compatibility Testing with Hydrazine. Jet Propulsion Laboratory Specification GMZ-50521-GEN, 15 December 1965.
- 4-22 Telecon, J. P. Stebbins/Boeing, and L. R. Toth/JPL, 18 June 1973.
- 4-23 Tolberg, W. E., et al, Chemical and Metallurgical Analyses of 6Al-4V Titanium Test Specimens Exposed to Hydrazine Liquid Propellant. Stanford Research Institute Report No. 951581-11, 15 April 1971.
- 4-24 Telecon, J. P. Stebbins/Boeing, and R. Hanna/Olin Corporation, Chemical Division, 6 June 1973.
- 4-25 Personal communication with F. S. Forbes, 1 June 1973.
- 4-26 Hickey, C. F., Jr., Aerospace Structural Metals Handbook.
- 4-27 DMIC Memorandum 201, "Compatibility of Materials with Rocket Propellants and Oxidizers." Defense Metals Information Center, Battelle Memorial Institute, 29 June 1965.
- 4-28 Salvinski, R. J., et al: Investigation of the Formation and Behavior of Clogging Material in Earth and Space Storable Propellants. TRW Systems Group Report 08113-6016-R000, October 1968.
- 4-29 Mars, J., "Compatibility Testing of C Series and J Series Stainless Steel Fittings", Memorandum, Rocket Research Corporation, 16 July 1969.
- 4-30 Earle M. Jorgenson Company, "Certified Test Report", Invoice Number 64265L, dated 20 December 1967; Forwarded to Boeing by L. R. Toth/JPL, 21 June 1973.
- 4-31 Telecon, J. P. Stebbins/Boeing and W. Cannon/JPL, 6 July 1973.
- 4-32 Gakle, P. S., et al: Improved Titan Predevelopment, Volume I, Propellant Development. Final Report BSD-TR-65-455, Aerojet General Corporation, February 1966.
- 4-33 Vango, S. P., "Determination of Carbon Dioxide Absorbed by Hydrazine," Jet Propulsion Laboratory, May 1973, (Preliminary, Unreleased).
- 4-34 Schmidt, E. W., Contamination Effects in Hydrazine Engines. Rocket Research Corporation Paper Presented to the Monopropellant Hydrazine Propulsion Systems Session. CPIA Publication No. 228, Volume IV, December 1973.

- 4-35 Axworthy, A. E., et al: Research on Hydrazine Decomposition. Rocketdyne Division, North American Rockwell Corporation, AFRPL-TR-69-146, July 1969.
- 4-36 Pullen, K. E., et al: A Method for the Prevention of  $N_2O_4$  Flow Decay. The Boeing Company, AFRPL-TR-72-121, December 1972.
- 4-37 Uhlig, H. H. and Lord, S. S., Jr., Amount of Oxygen on the Surface of Passive Stainless Steel, J. Electrochemical Society, 100, 216 (1953).
- 4-38 Uhlig, H. H., Corrosion and Corrosion Control. John Wiley and Sons, New York, N. Y., 1963.
- 5-1 "JANNAF Thermochemical Tables", Dow Chemical Company, Midland, Michigan.
- 5-2 Hollywood, L. P., T. R. Metz, and R. N. Porter, Storage Tests of Nitrogen Tetroxide and Hydrazine in Aluminum Containers, Jet Propulsion Lab., Pasadena, California, JR-32-1039, Jan. 15, 1967.
- 5-3 Vedder, W. And D. A. Vermilyea, Trans. Faraday Soc., 65, 561 (1969).
- 5-4 Begemann, S. H. A., and A. W. Smith, J. Electrochem. Soc., 117, 1440 (1970).
- 5-5 Clark, C. C., Hydrazine, Mathieson Chemical Corp., Baltimore, Maryland, (1953).
- 5-6 Young, L., Anodic Oxide Films, Academic Press, New York (1961), p. 166.
- 5-7 Smith, A. W., and Ann Pollock, Electrical Impedance of Aluminum Surface Oxide. Boeing Sci. Res. Labs., D1-82-0926, Sept. 1969, AD697117.
- 6-1 Pullen, K. E., Application of Radioactive Tracer Techniques to Flow Decay Problems. Boeing Company Report D180-12741-1, Contract NAS7-779, December 1970.
- 8-1 Denson, J. R., and E. A. Burns, Compatibility Testing of Space-Craft Materials and Space Storable Liquid Propellants. TRW Final Report 23162-6020-RU-00, JPL Contract 953486, February 1974.

APPENDIX A

LIQUID PROPELLANT TEST METHODS

TEST NUMBER 726.0

STATIC IMMERSION

JANNAF

Working Group on  
Propellant Characterization

March 1972

RECOMMENDED PRACTICES FOR STATIC IMMERSION  
TESTING OF MATERIALS IN LIQUID PROPELLANTS AND OTHER  
AEROSPACE FLUIDS

## TABLE OF CONTENTS

<u>SECTION</u>	<u>TITLE</u>	<u>PAGE</u>
1.0	General Considerations	1-1
1.1	Objectives	1-1
1.2	Definitions	1-1
1.3	Scope	1-5
1.4	Classes of Tests	1-6
1.5	Long Term Compatibility	1-8
2.0	Program Definition	2-1
2.1	Objectives	2-1
2.2	Type of Program	2-4
2.3	Available Information	2-13
2.4	Reactant Selection	2-13
2.5	Test Method Selection	2-19
2.6	Program Definition - Conclusions	2-21
5.0	Documentation	5-1
5.1	Test Identification	5-1
5.2	Test Objective	5-1
5.3	Test Description	5-1
5.4	Fluid Characterization	5-3
5.5	Material Characterization	5-4
5.6	Test Analysis Summary	5-6
5.7	Associated Documentation	5-7
5.8	Reporting Format	5-7

Members of the Fluids and Materials Compatibility Committee giving final recommendation and sanction of the method were:

Dr. Barry D. Allan, Army Missile Command, Redstone Arsenal  
Mr. John E. Branigan, Air Force Rocket Propulsion Laboratory  
Mr. William Buckley, Jr., Picatinny Arsenal  
Mr. G. W. Burdette, Naval Weapons Center  
Dr. Eugene A. Burns, Chairman, TRW Systems  
Mr. Mark T. Constantine, North American Rockwell, Rocketdyne Div.  
Mr. Donald L. Endicott, McDonnell Douglas Astronautics Co. - West  
Dr. W. David English, McDonnell Douglas Astronautics Co. - West  
Mr. W. A. Gogis, Naval Ordnance Station, Indian Head  
Mr. Larry H. Gordon, NASA, Lewis Research Center  
Dr. Richard Green, Boeing Aircraft Company  
Mr. Fred H. Meyer, Jr., Air Force Materials Laboratory  
Mr. Frank Piccirillo, Bell Aerosystems  
Mr. Leland B. Piper, Chemical Propulsion Information Agency  
Mr. Louis Raymond, Aerospace Corporation  
Mr. J. M. Robinson, North American Rockwell, Autonetics Div.  
Mr. Ural M. Robinson, LTV Aerospace Corporation  
Mr. S. D. Rosenberg, Aerojet-General Corporation  
Mr. Gordon Smith, NASA, Lewis Research Center  
Dr. A. W. Tiedemann, Hercules, Inc., Radford  
Mr. Louis R. Toth, Jet Propulsion Laboratory

## ACKNOWLEDGEMENT

The method recommended for Immersion Testing in Liquid Propellants was developed by coordination of the experience of laboratories from all sections of the aerospace community. Specific detailed recommendations were supplied by E. I. duPont de Nemours, Aerospace Corporation, Aerojet-General, NASA-Marshall Space Flight Center, McDonnell Douglas, Philco-Ford, Lockheed Aerospace, North American Rockwell TRW Systems, Jet Propulsion Laboratory, Air Force Rocket Propulsion Laboratory, Stanford Research Institute, NASA-Lewis Research Center, and Air Force Materials Laboratory.

The preparation of this method was conducted as an integral part of the Fluids and Materials Compatibility Committee and was coordinated as a sub-committee activity by Dr. W. David English, McDonnell Douglas Astronautics Company, West. Participants on the committee on the Immersion Test Method were:

Mr. Robert A. Biggers, Air Force Rocket Propulsion Laboratory  
Mr. John E. Branigan, Air Force Rocket Propulsion Laboratory  
Dr. Eugene A. Burns, TRW Systems  
Mr. Mark T. Constantine, North American Rockwell, Rocketdyne Div.  
Mr. Larry H. Gordon, NASA-Lewis Research Center  
Mr. Louis R. Toth, Jet Propulsion Laboratory



## FOREWORD

The objective of the JANNAF Working Group on Propellant Characterization is to encourage standardization of the testing methods which are used by the various agencies active in the development, evaluation and application of "solid" propellants. Wherever possible, the Working Group will recommend a test method which is capable of measuring a discrete or fundamental propellant property. Unfortunately, many factors relating to the physico-chemical characteristics of propellants cannot be determined on an absolute basis. In these cases it is often necessary to resort to tests whose results are apparatus dependent and which provide data that are meaningful only when considered relative to propellants whose characteristics are well known through practical use.

Such empirical tests can give comparable data only through the arbitrary standardization of test conditions. Although this standardization is one of the Working Group's primary tasks, it does not necessarily enhance the significance or value of a given test. In fact, it should be emphasized that the data obtained from tests may be dependent upon the established test conditions and may be inverted by other tests or test conditions. Each method when first issued is considered tentative. At reasonable intervals of time, and when sufficient justification occurs, revised methods are recommended. However, in the hope that the accumulation and correlation of sufficient empirical data may ultimately lead to a greater understanding of the fundamental properties of propellants, the Working Group strongly urges that users of the recommended test methods resist making any changes in apparatus or method which might lead to changes in the numerical values of data obtained. Suggestions of changes or improvements in apparatus or methods, however, are welcomed by the Working Group and may be sent to the CPIA for dissemination to the currently active membership.

RECOMMENDED PRACTICES FOR STATIC  
IMMERSION TESTING OF MATERIALS IN LIQUID  
PROPELLANTS AND OTHER AEROSPACE FLUIDS

1.0 GENERAL CONSIDERATIONS

- 1.1 Objectives: This document specifies conditions, parameters, and procedures for conducting immersion tests of materials with liquid propellants. The same considerations apply also to tests with other aerospace fluids. Specific details which are functions of particular test methods or propellants are covered in parts dealing with the particular subjects.

The objectives of immersion tests described in this document are (a) to supply engineering design data; and (b) for research into various interactions of materials and propellants. Thus the approaches are subtly different from similar methods for acceptance and quality control testing. For the latter methods, the appropriate ASTM Standards or MIL SPECS should be consulted.

For immersion tests, the total system of test fluid-material-test fixture-test container-instrumentation-test environment must be controlled, monitored, reported, and analyzed. Functional relationships between variables are sought, not just single point values.

1.2 Definitions:

The following definitions are included in the procedure to ensure uniformity, because some of the terms are currently used with several independent meanings. In some instances the meanings in these definitions are slightly different from those commonly understood.

- 1.2.1 Material (or Structural Material) - any solid, (amorphous or crystalline), polymer, elastomer, semi-solid, surface coating, etc., other than a liquid rocket propellant, aerospace fluid, or a gas, which is used in the construction or operation of a chemical propulsion system.

- 1.2.2      Liquid Propellant - a simple liquid (or its vapor), a mixture or solution of liquids, an emulsion, a thixotropic gelled liquid or a liquid with dissolved or suspended solids which is used in a rocket engine to produce thrust. Classes of liquid propellants include but are not limited to
- oxidizers
  - fuels
  - monopropellants
  - cold-gas propellants
  - externally heated hot-gas propellants
  - ionizable electric thruster propellants
- 1.2.3      Pressurant - a gas or vapor which is introduced into a liquid propellant container in order to raise the system pressure above the vapor pressure of the liquid propellant. It is usually, but not always, a chemically inert species. The pressurant may be brought directly in contact with the liquid propellant, or there may be a flexible or movable barrier which prevents direct contact but transmits pressure.
- 1.2.4      Gas - the state of matter which expands to fill a container completely and which cannot be caused to form a liquid at the temperature of interest by application of pressure, i. e., it is above the critical temperature of the particular system. The term "gas" will be applied to a mixture of gaseous constituents.
- 1.2.5      Vapor - the state of matter which expands to fill a container completely, but which is either in equilibrium with the liquid state or can be caused to form a liquid at the temperature of interest by application of pressure; i. e., it is below the critical temperature.
- 1.2.6      Aerospace Fluid - any fluid, other than a propellant or pressurant, used in aerospace systems. Such fluids include leak check solutions, calibration or reference fluids, lubricants, hydraulic and gyroscope liquids, cleaning solvents, purging and pneumatic operations gases, and decontamination liquids. Excluded are such fluids as atmospheric constituents, cutting oils, and porosity-detecting solutions used during manufacture.

- 1.2.7 Impurity - a substance, other than the specific chemical constituents or additives, which is dissolved in, suspended in, entrained in or otherwise transported by a propellant or other fluid. Note that by this definition such materials as water in  $N_2O_4$  are considered impurities, even when their concentrations are within a SPEC limit. However, water or other substance added purposely to a propellant in order to improve performance in some manner is not considered an impurity. Dissolved pressurant and products from material corrosion are included as impurities. However, suspended metal or hydride particles, purposely added to the propellant, are not impurities.
- 1.2.8 Contaminant - any substance forming a second phase which separates from the propellant and which is inadvertently formed in or introduced into a propellant system during construction or operation of the system. Included as contaminants are evolved gases and insoluble liquids. Particles formed by mechanisms or interactions related to service and functional operation are considered contaminants. These result from static or dynamic operation; examples are deterioration, wear, or corrosion of a material, and solids which precipitate from the propellant.
- 1.2.9 Reaction Product - a substance formed by a chemical reaction of a propellant, pressurant, or aerospace fluid. Included are combustion products from propellants, and products formed when fluid escapes from its tankage and reacts with the environs (e.g., HF from hydrolysis by atmospheric moisture of leaking  $F_2$ ), or those resulting from various environmental effects associated with the specific application such as extreme temperature, radiation from auxiliary isotope or nuclear power sources (i.e., radio isotope thermionic generators), or mission environments including zero gravity.
- 1.2.10 Additive - a constituent of a propellant or other aerospace fluid which has been specially added to modify some aspect of the behavior of the fluid. Usually it is of such a constitution that it would not be found naturally in the liquid. An example is the HF in IRFNA.

- 1.2.11      Specimen - the device, material, object, sample, coupon, component, system, etc., which is subjected to a test in order to observe or measure its behavior under the conditions of the test. A specimen may be the only item of its kind, or it may be a representative of a larger population. In this document, specimen will generally be restricted to solid phase materials.
- 1.2.11.1    Sample (or Random Sample) - refers to a specimen selected from a larger population by a randomizing sampling technique. The word sample should not be used when the whole population is tested as a unit, nor for a series of specimens cut successively from one end of a piece of material, etc. It is generally assumed that a specimen of fluid drawn from a homogeneous mass in a container is a true or random sample. In this document, sample will generally be restricted to fluid materials.
- 1.2.11.2    Coupon - refers to a material specimen which has been fabricated in a special shape for use in some specific test apparatus, e.g., a tensile coupon.
- 1.2.11.3    Test Article - refers to a material specimen, sample, or coupon, which is subjected to a test.
- 1.2.11.4    NOTE: Specimen is commonly used as a synonym for Coupon or Test Article, i.e., as a shortened form for Material Specimen. This usage is acceptable if the context clearly indicates the meaning, and no confusion with a specimen of the test fluid is possible.
- 1.2.12      Accuracy - the closeness of approach of a measurement or series of measurements to the "true" value of the quantity measured. Confidence in accuracy is increased if different observers and/or techniques arrive at values within the probable limits.
- 1.2.13      Precision - the closeness of approach of a number of similar measurements to a common value. It is measured in terms of deviation of individual measurements from the average.

- 1.2.14      Repeatability - a quantitative measure of the variability associated with a single test operator in a given laboratory using the same apparatus within a short interval of time.
- 1.2.15      Reproducibility - a quantitative measure of the variability associated with test operators working in two or more different laboratories.
- 1.2.16      JANNAF Statistical Procedures - a complete presentation of the official JANNAF definitions, symbols, and formulae for statistics, and instructions for round robin tests will be found in CPIA/WGAC Sections 800.0 to 850.0 of the Handbook (ICRPG), Working Group on Analytical Chemistry (of Solid Propellants), CPIA/H-1.
- 1.2.17      Other definitions are those commonly understood in science, technology and engineering.
- 1.3          Scope: Immersion tests are used to study changes in physical properties, chemical properties, mechanical properties and compositions of materials and of liquid propellants and other fluids due to mutual contact. Usually the changes that are of interest are those which affect the ability of the fluid and its system to meet their design performance. There are at least three separate testing cycles carried out on the specimens and/or samples in conjunction with the immersion tests. These are:
- 1.3.1      Determination of properties or characteristics by testing before immersion.
- 1.3.2      Determination of properties or characteristics by testing during immersion.
- 1.3.3      Determination of properties or characteristics by testing after immersion.
- 1.3.4      In general, the property determinations performed before and after propellant exposure are done by standard methods, and such methods will be referenced only and not detailed in this procedure. However, special considerations will be described. The immersion tests and any measurements made in the presence of the test fluids are described in this document. A matrix tabulation of the types of tests covered by the Immersion Test Method Procedure is given in Table I.

1.4 Classes of Tests

- 1.4.1 Compatibility Test - a test to determine the mutual interactions of two or more substances under the influence of more than one parameter; usually but not always done by an immersion test technique.
- 1.4.2 Immersion Test - a test or experiment in which a material specimen is immersed in a test fluid (vapor, liquid or both, including the interface) to determine the extent of mutual interactions which affect the properties of the material and fluid. The procedure may contact only one surface of the specimen with the test fluid.
- 1.4.3 Corrosion Test - a test to determine the effect on a metallic material of the interaction of the metal with one or more other substances under the influence of controlled test parameters. It is a restricted type of compatibility test.
- 1.4.4 Blank Test - a test carried out in the configuration of the regular test, with the same set of controlling parameters, but with one of the active species or test substances (material or fluid) not present.
- 1.4.5 Control Test - a test carried out in the configuration of the regular test series at one selected reference level of controlling parameters. It is conducted to establish a base line of behavior. In chemical analyses, a specimen of known composition is frequently used in control tests. These tests are sometimes called reference, base line or calibration tests by other authors.
- 1.4.6 Short Term Test - a test which lasts a maximum of 30 days.
- 1.4.7 Long Term Test - a test which lasts longer than 30 days.
- 1.4.8 Full Term Test - a test which lasts as long as the expected real system exposure.
- 1.4.9 Abbreviated Test - a test which is shorter than the expected real system exposure.

## TEST PROCEDURES INCLUDED IN IMMERSION TEST METHOD

187



- 1.4.10      Screening Test - these tests are conducted to determine whether a particular material-propellant combination will react vigorously under relatively weak initiation conditions, or is sufficiently stable so that it may be considered as a candidate for use in an aerospace system.

In static "Gross Reactivity" tests, a controlled specimen of the material is exposed to the propellant, and any reactions are noted. If the system seems stable, it is then subjected to a "Dynamic Initiation" test to determine if it is safe under conditions of shock, impact or friction.

- 1.4.11      Preliminary Test - these are initial short term tests for corrosion, mechanical property degradation, pressure build up, and other relatively non-violent interactions.

Analyses of the results of the preliminary tests supply information as to the important alterations of properties which were detected. These form the basis for study in the detailed immersion tests, if such tests are to be conducted.

- 1.4.12      Detailed Immersion Test

The detailed tests are designed to obtain information on the practical utility of material - fluid combinations. The tests are planned to develop specific information about extent and cause of interactions, and the expected useful life of materials or components fabricated from specific materials. Causes of failure, and the chemical reactions responsible, are also studied.

- 1.4.13      Verification Test

Verification tests are conducted to demonstrate that a complete assembly (component, subsystem, or system, etc.) will function in the required fashion over the total range of internal and external conditions defined for its service.

- 1.5          Long Term Compatibility

### 1.5.1 Objective

The objective is to advance the technology of material/fluid compatibility for long term mission applications or storage periods; specifically to discover or demonstrate acceptably inert structural materials for liquid propulsion systems that will have high reliability for periods of from one year to fifteen years when exposed in the mission or storage environments in contact with propellants. Current data for long term propellant compatibility are inadequate for the design and engineering application to liquid propulsion systems.

Long term compatibility investigations should be directed toward: (a) filling information voids; (b) understanding the implications of gross and subtle effects of operational storage periods of up to fifteen years; and (c) generating pertinent data upon which to base material selections for liquid propulsion components and/or feed system elements during design phases.

In summary, the objective is to determine the factors influencing or imposing the greatest impact on material compatibility and fluid stability for the purpose of establishing acceptably inert materials for design and construction of feed systems.

1.5.2 Accelerated Tests - Accelerated tests are substitute conditions for full term testing. It is essential that accelerated tests should not introduce mechanistic changes or other factors which are test-specific and do not relate to real effects encountered during long term exposures. Refer to Section 2.2.5.2 for a more detailed discussion.

1.5.3 Extrapolation From Abbreviated Tests - these extrapolations are intended to provide basic compatibility data based upon ultrasensitive measurements. A considerable variety of problems arise when attempts are made to extrapolate data from abbreviated tests, and care must be exercised in making these extrapolations due to possible mechanistic changes during the period of the test which may require a time period longer than that of the test before they become apparent. Refer to Section 2.2.5.3 for a more detailed discussion.

## 2.0 PROGRAM DEFINITION

### 2.1 Objectives

The general objective of an immersion test program is to generate data which define in predictable fashion the behavior of the materials and propellants when they are in contact. There are three major categories of these test programs. These are 1) generation of design data; 2) investigation of failures; and 3) correlation of properties and reaction mechanisms for research purposes. These are discussed below. The development of quality control or inspection test methods can be considered as a subcategory of property correlations.

#### 2.1.1 Design Data Generation

The objectives of design data generation are to supply information needed by design engineers about the properties and behavior of substances, propellants or materials, in order to design safe, efficient and economic systems. Such information includes mechanical properties, corrosion rates, chemical reactions, and many other types of data.

In laboratory studies and tests directed toward supplying new or confirming old information for designers, two points of view frequently clash. Some persons have a tendency to study interactions between materials and propellants under every conceivable permutation and combination of conditions. Some, on the other hand, have a tendency to be interested only in specific limited systems and conditions operant therein, and to ignore excursions and combinations of parameters. It is wise to ignore both extremes, and to plan a program which includes current needs, predictable short term future needs, and substitute systems or parameters for the cases when the first choices do not meet design minima.

It is necessary to be completely aware of operating requirements which have been defined or predicted for the system for which data are sought, including conditions which may develop in the system (real/test) as a function of time or system operations.

2.1.2 Failure Mechanism Investigation

The test objectives are straightforward. Some device(s) or system(s) failed to operate in the proper manner, and tests must be conducted to find out why.

In basic terms, failure to meet design performance can arise from many different sources, and these sources in turn result from:

- a) Changes in chemical properties or constitution of the propellant due to:
  - i. Changes in the molecular structure of the propellant.
  - ii. Introduction of new materials into the propellant.
- b) Changes in rate and amount of delivery of propellant or fluid including delivery at wrong time or no delivery at all due to:
  - i. Conversion of the propellant to a different physical state (solid or vapor).
  - ii. Loss of propellant due to major or minor leakage.
  - iii. Failure of propellant management system so propellant is in wrong location.
  - iv. Failure of propellant utilization or feed and transfer system (pumps, pressurization, bladders or valves).
  - v. Changes in dimensions of flow paths (opening up or blocking).

These changes are quite general, and in turn may arise from many causes. Thus, (b, i), the change in state of propellant, could be due to chemical changes, to failure of insulation, or to leaky valves which communicate to a vacuum, causing flash freezing. Similar degradation of performance can occur with pressurants and other aerospace fluids.

It can generally be asserted that if the properties of materials, components, or propellants change sufficiently to attain values outside of the expected statistical variation from normal values, degradation or complete failure of the systems will result.

In the majority of failures, considerable analytical investigation has already been performed before the test program is initiated, and the possible important parameters have been identified. On the other hand, if the item was properly designed on the basis of what appeared to be sufficient and accurate design data and operating condition predictions, it is likely that either some combination of factors occurring during service have interactions which were greater than a simple linear combination, or that some untested factor turned out to be important. The experiments to be conducted must then ascertain whether

- a) Existing data are accurate and complete
- b) Additional factors influence system behavior
- c) Combinations of certain factors accelerate deterioration.

Tests in which all specimens pass, or all fail, are of very little predictive use. Statistical and analytical procedures can only be properly applied when there are quantitative but not qualitative differences in the response of different specimens.

Successful performance of a failure mechanism study frequently results in the need for further design data generation. If this step can be foreseen, a combination of the two objectives in one test program may be the most efficient procedure.

### 2.1.3

#### Correlation of Properties and Mechanisms

The continuous development of new materials generates the need to determine how these behave in particular environments. The primary objective of the tests is to correlate the behavior with some controllable parameters inherent in the material, so that the proper direction to proceed in development of further improvements can be

determined. Correlation between tests of various types is also sought, in order to select the most economical test methods and to pick appropriate quality control methods and criteria.

Optimum design of property correlation tests is frequently difficult because only minimal quantities of materials are available. The tests should generally be conducted in a regime which shows the greatest differences in behavior due to changes in the material parameters. However, the effects of differences which are not under study must be carefully controlled so that test results are not confounded.

Study of reaction mechanisms in materials-propellant interactions is an extension of property correlation experiments. The tests are designed to develop information on the specific chemical and metallurgical processes which occur on the molecular and atomic level, and to correlate these processes with macroscopic changes which affect system behavior.

Mechanism studies usually involve very close control and accurate chemical analyses of the test fluids and specimens before and after test, and sometimes during tests. Metallographic and electron probe studies of the material specimens, and physico-chemical and various analytical chemical measurements of the test fluids are often involved; other similar approaches may be used.

## 2.2

### Type of Program

There are several types of programs in materials-propellant immersion tests. These include screening programs, preliminary programs, detailed programs and verification test programs. Long term compatibility programs are presented as a separate topic because of the special philosophy and the sophisticated analyses of test data which must be done. In many cases, the same basic test method may serve for any of the program types, the differences lie in the sophistication of the data collection.

Costs for programs rise rapidly with test sophistication. On the other hand, use of screening or proof test data for analysis is generally unsatisfactory, and uprating a less sophisticated program in the midst of conducting it because data of more basic character are needed usually results in higher costs and poorer data than if the more complex program were initially planned. It should be clearly understood what type of data are needed and the most economical type of test program to supply this data should be selected before planning the test details.

Also to be considered is the timing of the test program with relation to other activities. If the tests are part of a large system project, total project costs can rise alarmingly when materials testing is done too late. If selection of materials has not been completed by the time detailed design starts, the designers may be held up until the data can be supplied, or they may be required to proceed on a "risk" basis and either over-design or select unsafe materials. The only tests which should be necessary at this point in time are verification-testing of components in system-related operation conditions.

#### 2.2.1

##### Screening Program

A screening program is generally one which is designed to give "GO" or "NO GO" answers to questions about suitability under specific conditions of a materials-propellant combination. A "GO" answer indicates that the combination is suitable in terms of inherent stability to be subjected to further more detailed testing. Static and dynamic gross compatibility tests are included under screening. Static screening tests consist of exposure of controlled material specimens to the vapor and to the liquid phases of the test fluid under carefully controlled and safe conditions in order to determine whether vigorous reactions occur spontaneously. Dynamic test methods include ABMA Impact, Trauzl Block, Friction Initiation and Card Gap Shock tests and those contained in the Liquid Propellant Test Methods Manual. If easily initiated vigorous reactions occur which involve the fluid and material being tested, the combination is usually dropped from consideration and no further tests are conducted. However, many monopropellants will react when subjected to the dynamic initiation tests. It then becomes necessary to

distinguish between this normal reaction and an increased reactivity involving the material with the propellant, and to distinguish this latter case from a typical catalytic reaction. If increased reactivity is detected the deciding factors about system utility are such parameters as ease of initiation or violence of reaction.

If the screening tests are properly planned, no other hard data beyond "GO" - "NO GO" should be derivable. If numerical conclusions can be drawn, the test was more complex than a basic screening test.

False positive reactions between the test fluid and the test apparatus must not be confused with test material-fluid interactions. Blank tests must be run to check for the possibility of false positives.

It is sometimes possible to perform post-test analyses on a specimen to determine what has affected it. But in a typical screening test, the sample is not designed to be saved if the result is NO GO.

#### 2.2.2

##### Preliminary Program

A preliminary program is designed to obtain initial information about the type and extent of interactions between materials and propellants. This information is then used to plan the detailed test program. For instance, a number of metals may be tested in a particular corrosive environment for a short period of time. The corrosion rates are then calculated, and the types of corrosion which occurred are determined. Those alloys which have acceptable types of reaction (e.g. no pitting) and slower corrosion rates are selected for detailed study.

In selection of materials and conditions to be used in preliminary tests, a review of the information already available for the particular system and for analogous systems is very important. Many materials can be ruled out of tests at once; thus there is no reason to test tungsten in a new halogen fluoride. Knowledge of the behavior of materials and the characteristics of the propellant can also guide in the selection of types of interactions to be checked. If the test fluid is an electrical conductor, it is usually important



In detailed programs, test methods range from exact models of applications situations to very artificial conditions which, however, have been found to yield data which can be correlated with real behavior, or with some other parameter of interest. Acceleration of interactions by increased severity of test conditions (higher temperature, pressure, frequency) is typical of the artificial conditions. When such accelerated tests are conducted, it is important to demonstrate that the more severe condition does not cause a change in mechanism of interaction, which would result in invalid results.

Since the results of detailed test programs are to be used in prediction and correlation, the data developed must be complete and reproducible. Orders of magnitude and lists of relative effects are not sufficient.

In one area, the detailed program is inverted to become a method for testing of tests. This occurs in the development or selection of a standard method for quality control or inspection. In these cases, the information has already been developed that changes in some characteristic, C, of the substance correlates with a desirable or undesirable behavior in an applied system. It is now necessary to determine which test should be used to measure changes in C at the proper level of sensitivity in the most expeditious and economic fashion. Note that selection of the proper level of sensitivity is important; if it takes a change in C of 10% to cause an important system effect, one need not aim for a test which detects changes at the 1% level, although the 1% level data are usable. The converse is very definitely important. A test not sufficiently sensitive should never be used.

In the design of plans for detailed programs, it is usually wise to lay out a matrix of variables to be covered. This could initially consist of a set of lists of these variables: One list would cover specimen selection and design, a second would cover immersion conditions, a third would tabulate the physical conditions to be controlled in the test, others would cover chemical parameters, mechanical tests, dynamic changes, etc. The basic test design would then be drawn up to control all the parameters deemed of

primary importance, and to measure but not control secondary terms. Then an analysis would be conducted to determine the overall complexity of the test, considering how many independent values of each parameter should be tested. Of course, many of the parameters are not independent; thus pressure and temperature are completely coupled in a closed unpressurized container, once the quantity of fluid is selected. If the complexity is low--if only one or two parameters are to be varied over a few values, a straightforward test plan is drawn up in which each value of each parameter is checked. However, if the complexity is high--many parameters to be varied simultaneously, it is generally wiser to use an experiment designed on a statistical plan, in order to decrease the number of tests. If possible, the statistical plan should be one which allows for revision on the basis of experimental data as the program proceeds. Apparatus complexity is one of the factors which enters the decision as to whether a statistical plan is necessary. Thus a large variety of similar metal samples can be placed in a single test, and hence if the change in metal composition is the only parameter to be controlled, while, say, pressure, temperature and fluid volume are held constant, a statistical design may be unnecessary. However, testing one material at 4 temperatures and 4 flow rates each of which requires a separate test set up for each parameter change, will be more economically done if a statistical design is chosen.

#### 2.2.4

#### Verification Program

In a verification test, an article which has been designed and built for service in defined conditions is exposed to those conditions and its functioning is measured. The article may be anything from a subcomponent to a complete and complex system. In most verification tests, as much as possible of the complete range of defined service conditions is covered, and the response and behavior of the article is monitored throughout the test.

Except for the special categories of tests to destruction and life service tests, it is expected that the specimen article will survive the test, and the plan is based on such behavior. However, it is recognized that sometimes early in a design program, the first articles may not survive. When it is possible to do so economically, data collection to determine cause of failure may be included

in the instrumentation. This is not generally the case. Post test examination of the specimen plus analysis of the normally collected data are usually the only available resources. If they are not sufficient, a recycle through a detailed program aimed at failure analysis is usually required.

2.2.5 Long Term Compatibility Program

2.2.5.1 Full Term Tests

There is a serious lack of precise material-propellant compatibility data for long term storage of up to fifteen years with earth and space storable propellants. Important considerations relative to real time or full duration testing include:

- 2.2.5.1.1 Technical Utility - The results should be meaningful and not become outmoded by technical obsolescence as the result of state-of-the-art advances during the test.
- 2.2.5.1.2 Economics - Testing over long periods of time (five to fifteen years) can be prohibitively expensive. Any full term program should be carefully designed in all aspects in order to achieve a cost effective program.
- 2.2.5.1.3 Test Design - Careful analysis of the behavior of real systems in long duration exposures as functions of the system design and exposure parameters, and similar analysis of the behavior of the test system as it interacts with the propellant and materials specimen is essential for the proper design of the tests in order to obtain accurate data which are not confused with unwanted test-specific factors.
- 2.2.5.1.4 Post test characterization and documentation - These should be as thorough as practical to provide continuity and consistency in consonance with the procedural methods of this document in reporting pertinent factors, results, and test methods utilized during the active program.
- 2.2.5.1.5 Test constraints - The test constraints influence resulting from the test methods employed should be recognized and evaluated relative to the effects upon the final interpretation of results. Typically all phases are affected and major vs. minor considerations must be taken into account.

2.2.5.2 Accelerated Tests2.2.5.2.1 General

Accelerated testing is a method of determining the material-propellant compatibility under substitute short term conditions for real time testing. Accelerated testing, employing many different procedures, has evolved from the many different type programs conducted in the past. For example, specimens may be exposed to induced environmental conditions (such as high temperature, pressure, or g-loads) that exceed those required, and then examined after exposures. Results based upon these accelerated reactions are then correlated with actual data and applied to the design situation.

2.2.5.2.2 Rationale

The basis for accelerated tests is the assumption that "intensification" of one or more factors, (such as raising the temperature), will accelerate by the same ratio all reactions which normally occur in the test system without changing any of the reaction mechanisms or causing any new reactions. Thus compatibility effects can be obtained in shorter time periods.

This assumption of linear behavior is only approximately true even over limited ranges of variation for system parameters. Hence the test designer must not exceed these limits or false effects will occur.

2.2.5.2.3 Uses and Constraints

The test methods employing accelerated means to simulate real time reaction products and interactions are of particular importance to permit earlier assessment of materials compatibility information. To ensure that applicable data for design purposes is obtained, the test designer must completely understand the relation of the test conditions to those that are being simulated. This is difficult to achieve from both a theoretical and engineering application standpoint, hence the influence of environmental simulations should be carefully evaluated and controlled in order to preclude or reduce the number of overlapping interactions when using this test technique.

It is essential to demonstrate that the accelerated test environment selected does not introduce new reactions nor change the relative rates of different reactions occurring in the test to such an extent that the internal test environment is no longer a satisfactory model of the real system.

2.2.5.3 Extrapolation from Abbreviated Tests

2.2.5.3.1 General

This procedure is directed toward investigation, analysis, and experimental testing for the purpose of establishing fundamental data and generation of criteria based upon relatively short duration tests instead of full term tests.

In order to obtain accurate results, the extrapolation methods used should be applicable for predicting material-propellant compatibility performance, not only on a relative basis but also on an absolute time-lapse basis. These methods must be capable of indicating, by extremely sensitive measurements, the effects of interactions, combinations, dissimilarities, activation sites, etc., between the specimen and fluid and conversely the fluid and specimen.

2.2.5.3.2 Uses and Constraints

Ideally these techniques will identify and discriminate between different kinds of time dependent gross and subtle effects. The rates at which the reactions proceed are dependent upon a variety of different parameters and mechanisms. Test and measurement techniques should provide an index to the rate of dissolution of specimen constituents into the fluids; decomposition rate of the fluid; and reactions on the specimen, surfaces and interfaces. Such identification of operational compatibility interactions, combined with known magnitudes should provide accurate data for extrapolation to long term (up to fifteen years) application. Thus the suitability of a material can be evaluated and correlated with full term data with far more precision than with any other available method.

In many material-propellant systems, initial reaction rates are very high but in a short period of time the reactions slow down dramatically. This process is often called passivation. A reverse behavior of the rates sometimes occurs--it is called induction. If either takes place, then the reaction rates extrapolated for long term exposures should be the steady state rate, and the initial period should be subtracted from the steady state rate and reported separately.

## 2.2.5.4

Summary

The development of real-time data about the effects of long duration exposures is highly desirable. However, in many cases such programs are not feasible because of cost considerations, schedule demands, or other factors. Data must be obtained in accelerated tests or extrapolated from abbreviated tests. Great care must be used in developing data by such techniques, because small errors are quickly magnified by a sort of "lever" effect. Table II consists of a list of some of the important factors in long term compatibility considerations. Many of these factors apply to tests and to real systems, both, but often not with the same weighting. The list is not supposed to be complete, and the test designer and conductor must ensure that any additional factors in the real or test system of interest are not overlooked.

## 2.3

Available Information

An annotated bibliography of immersion testing is being published as a separate JANNAF document. It deals with published test methods, including standard methods, recommended methods and non-standard methods used in specific studies, and also with important leading references to published data on studies of the interaction of structural materials with propellants and aerospace fluids.

## 2.4

Reactant Selection

The applications of the test program limit to definite classes or groups the materials and fluids which may be selected. The particular objectives, type of test, and test procedures adopted then define the selection of specific reactants.

Table II

FACTORS OF POTENTIAL IMPORTANCE IN  
EXTENDED DURATION COMPATIBILITY

Extended Duration Exposure (Test or System)

Perfusion through organic materials (test fluid/outside atmosphere)  
Seal leakage  
Changes in rate at different locations due to thermal stratification  
Effects of venting  
Concentration changes due to evaporation of volatiles  
Slow composition changes in fluid (decomposition of  $N_2H_4$  or  $N_2H_5NO_3$ )  
Slow changes in material due to mechanical operations  
Low level galvanism  
Creep of materials  
Effect of surface active agents in propellant and on materials  
Surface to volume considerations considering accumulation of reactive products.

Accelerated Tests

Effect of temperature (pressure, etc.) on all reaction rates  
Effect of temperature (pressure, etc.) on reaction mechanisms  
Diffusion control of heterogeneous reactions (agitation speeds reactions)  
Sequential reactions  
Solid state diffusion  
Effect of temperature changes on vapor phase composition and evaporation processes, fluid density, and cavitation  
Solubility changes for slightly soluble reaction products

Extrapolation from Abbreviated Tests

Passivation  
Induction  
Changes in concentration of reactive or inhibitory species  
Very slow reaction paths

It should be noted in passing that tests described as Long Term may actually be Abbreviated Tests in comparison to actual Extended Duration operation of a system.

The basic ground rule for reactant selection is that the reactant should be the same as that anticipated in actual service. If this is not feasible or practical, simulants may sometimes be substituted. Their selection should be on the basis of reactants which have similar chemical or physical or mechanical properties, or appropriate combinations. The basis of selection for reactant simulants will be primarily dictated by the objective of the investigation, but, in general, the desired independent variables to be simulated shall include the following:

- a) temperature range
- b) phase state
- c) degree of reactivity
- d) susceptibility to external variables
- e) concentration
- f) chemical properties
- g) physical properties
- h) mechanical properties

#### 2.4.1

##### Test Fluids

Most fluids can be obtained in a variety of grades. In order of increasing quality (purity) these are commonly listed as technical, commercial, commercially pure, chemically pure, reagent, high purity, spectroscopic, electronic, and ultra pure. Specifications for aerospace fluids are based on the requirements of the system in which they are used, and may be equivalent to any one of the grades, often with special requirements in addition. Most propellant specifications are about equivalent to commercially pure or chemically pure grades.

The category of test will determine the choice of fluid. In screening and preliminary tests, commercial to commercially pure or SPEC grades will do, without further analysis or definition of properties or constituents. Verification programs should employ the SPEC grade which will be used in normal service, with normal SPEC analysis.



For detailed programs, the complete constitution of the fluid should be determined by accurate chemical analysis, not just MIL SPEC analysis procedures. Design data programs should be conducted with propellant grade or equivalent fluids, but, again, the fluids should be analyzed as completely as possible. In property correlation and reaction mechanism studies, the purest available fluid should be used, and analyzed thoroughly. When impurities or other constituents are required in the fluid to study their effects, these should be added in weighed amounts to the pure base fluid. The modified fluid should then be analyzed again. All test fluids must be traceable by lot number to the manufacturer.

As previously stated, the selection of the proper reactant is primarily dictated by the test objective. In the majority of the cases every effort should be made to duplicate the real reactant as closely as possible. Consequently, the chemical and physical properties of the test fluid should be the same as those in the naturally occurring solution or, as in the case of most propellants, those taken directly from some plant process, i.e., in an "as received" condition.

Unfortunately, it is not always possible to obtain the "exact" test fluid for investigation, and availability of similar test fluids dictates the selections. In such cases, it must be determined which independent variables are of prime importance to the investigation and on this basis the test fluid simulant should be selected. In making these selections, care should be taken to insure that conservative results will be obtained.

Another important consideration in the selection of test fluids is the effect of external variables. The effects of aeration and vibration may become predominant and must be accounted for. Conversely, if this variable is not predominant, then special consideration should be given to keeping the test fluid saturated with an inert gas and in a state of quiescence.

Based on the above it becomes quite evident that the selection of the proper test fluid, either "exact" or "similar" is dictated by the test fluid as the controlling variable in the test and not subject to some uncontrolled variable.

## 2.4.2

Pressurants and Dissolved Gases

Equally important in reactant selection is the selection of pressurization gas systems which will prevent all foreseeable system contamination. This is of prime importance where the test fluid is a high energy propellant.

Two cases where a pressurant gas is used in conjunction with the main test fluid must be considered. The pressurant may be present as a required factor in the test design, or it may be present because it is not prohibited and it makes manipulation of the liquid phase more convenient. This latter case includes gases, even air, dissolved in the liquid before it is introduced into the system, even though the free pressurant is not introduced directly into the system.

Pressurant selection must follow the same rules as those for test fluid selection with regard to impurities, which typically include  $O_2$ ,  $CO_2$  and  $H_2O$  in many pressurant gases. The solubility of the pressurant in the liquid propellant should be known, and the degree of saturation measured.

Pressurants can interact with the test liquid to change compatibility effects. Thus dissolved gases seriously affect cavitation behavior. The impurities in a pressurant can have large effects, since they may react with the propellant to give corrosive materials. These possible effects must be considered in the test and system design.

The best way to ensure the high purity pressurant gases is naturally to obtain them in the liquid state and then vaporize the gas as needed; however, the pressurants commonly used at the present, e. g., nitrogen and helium, are usually stored as gas.

Pressurant gases for use with test fluids should meet the following minimum specifications:

- a) Helium - AF Grade A No. 7500-156410
- b) Nitrogen - MIL-P-27401A

Other pressurants, e.g. argon, CO<sub>2</sub>, etc., should meet their respective MIL SPECS where applicable. Generally, the wetness requirements for pressurants should be a minimum of -60°F dew point. However, in the case of extremely reactive test fluids, e.g. fluorine, the minimum dew point should be -100°F.

Hence, it not only should be the availability and inertness of the pressurant which dictates its selection but also the susceptibility of the pressurant to absorb contaminants, primarily moisture, either in storage or use.

#### 2.4.3

##### Specimen Materials

Screening and preliminary tests frequently make use of many different test materials, but in the more detailed tests, the number of materials is greatly reduced. The program objectives, systems design requirements or test constraints due to material interactions put narrow limits on the selections which may be made. Typically, tests in one series are restricted to a few alloys of similar composition. Instead of variation in the materials composition, variation in its condition, finish, joining methods, plating, stress load, and other factors which relate to fabrication, joining and structural uses are frequently studied.

The material composition and condition should be documented by whatever methods are appropriate. The documentation should include the fabrication history of the specimens, specifying location and orientation on the billet, sheet, or other stock from which they were cut. All materials must be traceable by lot number to the manufacturer.

Combinations of materials of different composition may show unexpected interactions, and should be avoided in testing, unless study of such interactions is the goal of the test.

Tests of components and systems are usually restricted to those materials which have been incorporated by the designer. In this case, the test conductor has no control over the materials and their condition in the test objects. Therefore he should request accurate documentation from the designer and fabricator.

Again, many of the requirements given above for test fluids are applicable to the material selection. The material should be the same as that contemplated in service, if possible. If similar materials are needed, the criteria on simulant selection should be applied with particular emphasis on physical and mechanical properties as well as degree of reactivity.

#### 2.4.4 Test System Materials

It may not only be the fluid or specimen which are the reactants. Test results may be invalidated if other substances, such as the container material, undergo a reaction. The potential effects of an erroneous material selection on a corrosion test is obvious as the large surface area of the susceptible container material could completely negate the results of the test on a coupon of smaller surface area.

#### 2.4.5 Summary

Selection of materials as reactants is critical not only to the desire of having relative inertness in a system but also to simulate as closely as possible the real service material environment on the basis of temperature, strength of materials, etc.

#### 2.5 Test Method Selection

##### 2.5.1 Test Type

The main requirement to be met is that the method of test selected yield meaningful results consistent with the basic objectives noted in Section 1.1, and the specific objectives discussed in Sections 2.1 and 2.2. The numerous specimen types, test methods, and possible interactions may be grouped under the two generic categories discussed below.

##### 2.5.1.1 Static Test

This method involves exposure of the specimen under test to the liquid, liquid-vapor, and liquid-vapor interface phases under static conditions (that is, with no relative motion applied and controlled as a test parameter).

A subcategory of static test is one in which some portion of the system is at an energy level above the rest of the system, but in which this excess energy does not cause dynamic conditions to develop. Stress corrosion and compression set tests are typical examples. In terms of basic mechanistic considerations these tests are quite different from simple static tests; however, the test procedures, other than the application of the specific load, are usually identical with procedures for static tests.

2.5.1.2 Dynamic Test

This method involves exposure of the specimen under test to dynamic conditions, typically flowing propellant, environmental simulation, or functional operation as in service. This document is a procedure for static immersion testing and it does not deal with dynamic conditions except for a few special cases.

2.5.2 Apparatus and System

The apparatus and system utilized to carry out and support the testing activities should be simple, and should result in a minimal influence on the test specimen and test results.

The design and selection of test apparatus must include consideration of the effects of the external environment on the test and on the system for which the test data are needed. Such factors as vibration, leakage to the interior, shock, stray magnetic fields, or humidity may have to be controlled. In general, the internal test environment is analyzed to determine to what variables it is sensitive, then the environment of the test is controlled to hold these variables constant at some selected level, which may be zero.

2.5.3 Instrumentation

In general the test program will require instrumentation for measuring specified parameters. The instrumentation should be as simple as possible and should result in a minimal influence on the results of the test. It is important that the sensors, data output systems, and intermediate devices should be stable over the duration of the test. All instrumentation must be calibrated and traceable to the National Bureau of Standards. The precision and accuracy

should be appropriate to the controls applied to the test, and to the accuracy needs for application of the data. Excessive accuracy gains nothing, and costs a lot.

#### 2.5.4 Test Variables

A knowledge of all the properties including the composition of every element involved in the test program is desirable in order to make both the resolution and reproduction of the data as reliable and accurate as possible.

The number and level of testing depends upon the particular program requirements. The many possible variables should be carefully analyzed so that only the critical test variables, and their levels are established and adhered to during the program.

#### 2.6 Program Definition - Conclusions

Compatibility test procedures, costs, results, and data utility are under the strong influence of a wide variety of parameters. It is necessary to identify and define the specific important parameters in order to design the most cost-effective test program which meets the program objectives.

APPENDIX B

PREPARATION OF 6A1-4V TITANIUM RESIDUE  
SAMPLES FOR ANALYSIS

As Performed By The

Lawrence Livermore Laboratory  
Livermore, California

PRECEDING PAGE BLANK NOT FILMED

#### BOEING SAMPLE PREPARATION

##### Reagent:

3N HCl prepared from quartz distilled HCl and Biomed distilled water.

##### Conditions:

1. Reagent Blank: 2 milliliters (ml) 3N HCl directly in Durathane bag
2. Sample Blank: 2 ml reagent rinsed in Boeing container then put in Durathane bag.
3. Spike sample: 1 ml of spike solution containing 2  $\mu$ g each of Al, V, Ti, were dried in a Boeing container. 2 ml of reagent used to take up residue and transferred to bag.
4. Spike Reference: 1 ml spike solution and 2 ml reagents directly into Durathane bag.

##### PROCEDURE:

1. Small Durathane bags were soaked in 6N HF for 2 hours, rinsed with water (distilled) and soaked with 3N HCl for 2 hours, then rinsed well with distilled water. Bags were dried in freeze drying apparatus.
2. Freeze drying samples: Reagents were pipetted into the Boeing container, dissolving the residue. The solution was then quantitatively transferred to the Durathane bag which was held in a polybag. A small Durathane bag was put over the first one.
3. Samples were frozen in dry ice and  $\text{LN}_2$ , placed in freeze drying apparatus and pumped until dry.
4. Durathane bags were then activated in the reactor and counted.

PRECEDING PAGE BLANK NOT FILMED